CALCIUM CARBONATE INTERACTION WITH ORGANIC COMPOUNDS

by

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Abstract

Dissolved organic compounds interact with the surface of calcium carbonate minerals and effect simple inorganic equilibration between solution and solid. Organo-carbonate associations form between stearic acid and calcite and dolomite, and between albumin and aragonite, calcite, and Mg-calcite.

When stearic acid interacts with these minerals in hexane solution, there is evidence that the association results in a complete monolayer on the calcite surface and in half of a layer on the dolomite surface. Interaction is restricted to the calcium sites of the solid and the carboxyl group of the stearic acid. The same relationship exists between calcium and reactive organic sites when stearic acid and carbonate minerals interact in aqueous solution; however, the amount adsorbed is not sufficient to form a complete monolayer of pure stearic acid. Instead, the ion activity products of

$$pCa^{++} + pHCO_3^- + pStAc$$

$$pCa^{++} + pOH^- + pStAc$$

indicate that the aqueous solution is perhaps in equilibrium with one of two surface complexes with the above composition. Hydrated surface complexes appear to be large enough to completely cover the surface of carbonate minerals in aqueous solution.

At concentrations of approximately 25 mg of albumin per liter of water, carbonate minerals appear to adsorb sufficient albumin so that a complete monolayer is likely to form. At high concentrations, and with increasing time and pH, multilayers or unoriented aggregates of albumin form on calcite and aragonite surfaces. Dissolved alanine does not associate with carbonate minerals at pH 6.12 and pH 9.87.

Organo-carbonate associations affect the calcium carbonate equilibrium in solution by physically isolating the mineral surface and by reducing the surface free energy of the solid. Selective association with calcium sites and equilibration of the surface complex with the solution both could prevent simple dissolution reactions.

In the natural environment, adsorbed unspecified surface-active compounds cause the total dissolved carbon concentration of the uppermost sea surface layer to increase up to fivefold as compared to the bulk surface seawater. Between 10% and 15% of this surface-active matter can be removed from seawater by adsorption on calcite surfaces. Organic compounds containing phosphorus are involved in this solid-seawater interaction.

At low calcite to seawater ratios, the adsorbed surface-active organic matter is visible on the surface of calcite and can be stained by Methylene Blue. The artificially produced organic coatings look the same as those observed on natural suspended carbonate minerals. At intermediate and high ratios, the seawater is depleted of surface-active organic matter. This allows uninhibited inorganic equilibration between seawater and carbonate minerals.

Surface seawater, deep water, and interstitial water show inorganic equilibration at different calcite to seawater ratios. These ratios are constant for one seawater sample whether equilibrium is approached from under- or oversaturation.

Recent carbonate sediments from the Bermuda platform show stainable organic coatings. The sediments do not interact with undersaturated seawater, but dissolve after organic matter has been removed by H_2O_2.

The natural stability conditions for organic coatings are unknown, but Pleistocene, Jurassic, and Mississippian carbonate rocks contain stainable organic matter. In samples from the Bermuda Pleistocene, organic matter is localized on the surface of uncemented carbonate particles and in pore spaces of carbonate rocks. The organic matter is stained with Methylene Blue in the micrite envelopes of an Upper Jurassic limestone sample from France and in pore space linings of a sample of Mississippian dolomite from Indiana. All organic matter encountered in pre-Recent rocks is associated with clay minerals which interfere with the Methylene Blue staining technique. Because of this interference, conclusions concerning effects of organic coatings on limestone diagenesis are only tenative. It is believed that organic coatings as well as organo-clay associations on the surface of carbonate mineral particles are responsible for lack of equilibration. This is evident from the textures and mineralogy of carbonate rocks. Lack of grain enlargement (recrystallization), persistence of metastable carbonate phases (aragonite), and blocking of calcite precipitation nucleii during cementation of limestones are the major diagenetic processes which are affected by organo-carbonate associations.

INTRODUCTION

The behavior of calcium carbonate in various sedimentary environments is an appealing, but treacherous, subject for quantitative geochemical treatment. It is appealing because of the apparently simple composition of the major minerals involved and because of the rapid and easily reversible reactions that occur in some laboratory experiments. But the interrelationship of biological, chemical, and physical factors in the marine environment actually so complicates the application of geochemical principles that few valid predictions can be made concerning formation, dissolution, and stabilization of calcium carbonate minerals.

Organic compounds in the ocean interact with these minerals. The properties of the resulting organo-carbonate associations may explain the variable behavior encountered in carbonate geochemistry. Some of the related problems are outlined below; they concern aspects of carbonate minerals in chemical oceanography, biogeochemistry, and petrology.

Problem outline

Supersaturation--. The first significant problem in evaluating physico-chemical precipitation is to explain the apparent supersaturation of surface seawater with respect to calcite. Wattenberg (1933), and MacIntyre and Platford (1964) illustrated the saturation state of Atlantic surface waters with respect to calcite by contouring points of equal degrees of supersaturation. The saturation state shows bilateral symmetrical distribution from the Sea of Labrador to the Falkland Islands, with a maximum of 300% saturation in tropical latitudes and 150% at high latitudes. Cloud (1962) calculated 180% saturation with respect to calcite for surface waters in the Straits of

Florida. Garrels and Thompson (1962) applied activity coefficients to the calcite equilibrium for calcium and carbonate in seawater. The activity coefficient for calcium was obtained from the mean salt method; for carbonate, it was calculated at the ionic strength of seawater from the Debye-Hückel theory. Garrels, Thompson and Siever (1961) also calculated the distribution of complexed species of calcium and carbonate and found that the effective concentration of calcium in seawater is reduced by 9% and that of carbonate by 91%. They concluded that seawater at 25°C and 1 atmosphere pressure is 150% saturated. Krauskopf (1967), reviewing the present state of knowledge, noted that the discrepancy between ion activity product and solubility product of calcium carbonate in seawater is not wholly removed. However, he leaves open the question of whether or not seawater is supersaturated by saying that the discrepancy is as far reduced as we can expect when applying geochemical principles to seawater as a complex solution.

Saturometry--. Saturometry measurements on surface seawater by Weyl (1961), Schmalz and Chave (1963), MacIntyre (1965), and Chave and Schmalz (1966) demonstrate supersaturation of these waters with respect to calcite. The same techniques applied to interstitial waters from neritic carbonate sediments indicate slight supersaturation and saturation with respect to calcite (Berner, 1966a). However, Recent carbonate sediments are mixtures containing at least 50% aragonite and/or a spectrum of Mg-calcites of high solubilities (Land, 1967; Schmalz, 1967). With respect to these highly soluble phases, the interstitial waters are undersaturated.

Source of carbonate sediments--. Physico-chemical precipitation of calcium carbonate from seawater should produce a mineralogically and

chemically defined precipitate, considering that the composition of seawater is almost constant. However, a compilation of 758 mineralogical analyses of Recent carbonate sediments by Land (1967) demonstrated the wide variety of mineral phases deposited. All of the samples contain more than 50% metastable minerals under natural conditions. Cloud (1962), Broeker and Takahashi (1966), and Milliman (1967) consider the aragonite mud of the Bahama shelf to be a physico-chemical precipitate from seawater.

However, Lowenstam (1955) and Lowenstam and Epstein (1957) showed that aragonite needles from Penicillus sp. are morphologically and chemically indistinguishable from aragonite which is precipitated inorganically. They emphasized the importance of biochemically-produced carbonate sediments. Stockmann, Ginsburg, and Shinn (1967) recently showed that a few dominant species of aragonite-secreting algae may well have produced all the fine-grained aragonite sediment in South Florida within the last 4,000 to 10,000 years. Neumann and Land (in preparation) found similar results for the Little Bahama Bank.

Rock textures and mineralogy--. Ancient chalks and other fine-grained limestones have not recrystallized to coarser fabrics. Pantin (1965) and Weyl (1958, 1964) calculated that these sediments with a grain size of 3-10 microns should recrystallize within hours or days.

Many calcite crystallization nucleii are available in carbonate rocks; however, this nucleation density does not influence the growth of the cementation mosaic (Bathurst, 1964). Hall and Kennedy (1967) report several hundred examples of preserved skeletal aragonite from Tertiary and Mesozoic rocks. The preservation of this metastable calcium carbonate phase indicates persistent lack of equilibration.

Summary--. Inhibition of physico-chemical reactions involving the calcium carbonate equilibrium in today's oceans and sedimentary environments is indicated by the following observations: supersaturation of surface seawater with respect to calcite, lack of diagenetic transformation in sediments and rocks, absence of physico-chemical calcium carbonate precipitates in sediments, and the production of most of the Recent carbonate sediments by organisms.

Relevant work

Suspended carbonate minerals --. The suspended mineral load and the ocean waters represent a geochemical environment which provides basic information on the problem of seawater-carbonate interaction. According to Chave (1965a), the suspended carbonate particles are not in direct contact with seawater because of enclosure in organic aggregates that cause physical isolation of the carbonate surface. Wangersky and Gordon (1965) also report association of organic matter with suspended carbonate minerals from open Atlantic surface waters.

Chave and Suess (1967) describe carbonate minerals in both under- and oversaturated seawater off West Florida. They propose organo-carbonate associations to account for the lack of equilibration between the minerals and seawater. Such organo-carbonate interaction blocks any new nucleation of calcium carbonate precipitates. Therefore, seawater should remain supersaturated for indefinite periods of time. Organo-carbonate associations may also explain the persistence of metastable carbonate minerals in undersaturated interstitial waters and the general absence of carbonate precipitates. They may inhibit recrystallization of fine-grained sediments and cause distinctive grain textures in limestones.

Plan of work

Review of organo-mineral associations--. A general review of organo-mineral associations in nature precedes the experimental treatment of the proposed organo-carbonate interactions. Industrial applications of organo-carbonate associations encountered in ore flotation and in chromatography provide experimental experience with the proposed interacting system.

Model experiments--. Organic compounds are adsorbed from solution by various carbonate minerals. Organic ionic species and surface-active compounds, with and without ionic properties, interact with various carbonate minerals. The molecular structure of selected coatings is interpreted from the model experiments. A discussion of the effects on carbonate dissolution and precipitation concludes Chapter II.

Organo-carbonate interactions in seawater--. Application of these experimental observations to the natural environment of seawater and sediments constitutes Chapter III. The interaction of carbonates with organic matter of the sea, and especially of the sea surface, is discussed. A special procedure measures the effective coating of free carbonate surfaces by dissolved organic compounds in different water masses. Biochemical and histochemical methods are used to study the chemistry of natural compounds involved in coating. Environmental and ecological implications are considered in a discussion of a continuous cycle of surface-active compounds in nature.

Organo-carbonate associations in sediments and rocks--. Chapter IV deals with the influence of natural organic coatings in sediment and rock constituents. Organic coatings of suspended carbonate particles

and neritic carbonate sediments are directly identified by staining techniques. The coatings influence the solubility of carbonate minerals in undersaturated interstitial waters.

Finally, the principal findings in the Recent environment of carbonate deposition are applied to Pleistocene, Jurassic, and Mississippian carbonate rocks. With staining techniques it was attempted to observe the remains of organic coatings directly. Effects of initial organic coatings are inferred from carbonate rock textures and compositions. Some observations on complexing of metal ions and dissolved organic compounds in seawater indicate concentration of trace elements in carbonate sediments. This aspect is not developed in detail, but it is a direction in which future investigation might lead.

Weyl (1967) and Berner (1966a, 1966b, 1967) propose an alternative hypothesis which is analysed, discussed, and compared with the organic coating hypothesis proposed here.

I. ORGANO-MINERAL ASSOCIATIONS

The following questions are considered during the study of the proposed organo-carbonate interactions:

1. What organic compounds interact with carbonate minerals?
2. How are organic molecules arranged on the mineral surface?
3. What are the configuration, content, and dimension of layers of organic compounds associated with the mineral?
4. Which sites on the carbonate minerals and organic compounds interact with each other?
5. What is the bond between the mineral surface and the organic compound?
6. How stable is the association under natural conditions?
7. How is the solubility of carbonate minerals affected by organic associations?

Organo-mineral associations in nature and industrial applications

Various branches of fundamental and applied research have contributed theoretical knowledge, some ingenious experimental procedures, and descriptive material useful in understanding organo-mineral associations.

Soil science--. The importance of organo-mineral associations was discovered by soil scientists. The influence of humic acids upon the ion exchange capacity of soil minerals was noted as early as 1920 (Gedroiz, 1920). Sokolowsky (1919) and Blank (1931) recognized that the physical properties of soils improved through association of organic compounds and soil minerals. Specific bonding formation between selected soil minerals and defined organic compounds is studied by infrared spectroscopy in soil science research (Tahoun and Mortland, 1966; Bremner, 1951). In the Soviet Union, interactions between synthetic polymers and soil minerals for the improvement of physical properties of soils are proposed on a technical scale (Taymurozova and Ignatyeva, 1965; Fiedler and Reissig,

(1964). Applications of organo-mineral complexes are summarized by Nahin (1963) in publications of the 10th Soil Science Conference. The study of organo-clay complexes has become an independent branch of clay mineralogy.

Flotation--. The flotation method in ore-processing, introduced in 1940, started a period of intensive research on organo-mineral interactions (Sebba, 1962). The prime objective of such studies was to determine the stability of organo-mineral complexes. A vast number of so-called mineral collectors have been described. They are classified according to their reactive groups as xanthanes, mercaptans, dithiophosphates, carboxylic acids, and amines. Table I shows the structural formulas of major groups of mineral collectors.

Research on carbonate, fluorite, and apatite flotation by oleic acid and on bonding between amines and silicates has geochemical implications (duRitz, 1965; Lidström, 1965; Smith and Utley, 1968).

An excellent compilation of current work in this field is given in the Proceedings of the Second Scandinavian Symposium on Surface Activity, edited by Ekwall, Groth, and Runnström-Reio (1965).

Geosciences--. Organo-carbonate associations and organo-clay complexes have geochemical and sedimentological importance. Faber and Krejci-Graf (1936) postulated the association of stearic acid and carbonates as a model for the retention of organic compounds in carbonate sediments. They thought these compounds constituted protopetroleum; however, their experiments and observations were negative.

The origin of petroleum has been a subject necessarily concerned with organo-mineral associations. However, only the presence and abundance of these associations have been described. Basic questions such as the nature of the bonding mechanism, stability conditions, and the

structure and configuartion of the associated organic molecules have barely been investigated (Baker, 1962; Brooks, 1954; Krejci-Graf, 1963). Such questions cannot be answered by studying only the given natural environments, the oceans and rivers in which organo-mineral associations exist. Studies in selected systems under carefully controlled conditions of solution concentration, time, pH, and temperature may yield a better insight.

Smith and Bader (1961) investigated the organo-mineral associations of amino acids and carbohydrates with montmorillonite, kaolinite, illite, and quartz. They established that the association depends upon:

molecular weight of organic compound
functional group of organic compound
surface area of mineral
surface activity of mineral
pH of system
chlorinity of system
temperature of system
pressure of system

They postulated a complex clay-organic gel formation on the surface of the mineral. The initial stages of formation are physical and chemical adsorption processes. One characteristic phenomenon encountered in the study of organo-clay complexes is the effect of organic compounds on the cation exchange capacity of clays. McCrone (1967) shows that between 86% and 97% of the cation exchange sites of estuarine muds are located on the oxidizable organic fraction. However, Bader and Jeffrey (1958) showed that organic compounds reduce the ion exchange capacity of marine muds.

Chromatography--. In an historic experiment, Tswett (1906) used powdered calcium carbonate to separate plant pigments from a series of organic solvents by adsorption. He coined the term chromatography.

Surface chemical principles

General surface chemical concepts and terminology are adopted from Adamson (1960), Davies and Rideal (1961), Gregg (1961), and Kipling (1965) for the description and study of the proposed organo-carbonate mineral interactions. Physical and chemical adsorption are considered under the collective term of sorption. Sorption and ion exchange are the two major types of solid-liquid interactions.

Physical adsorption--. Physical adsorption results from electrostatic and dispersion forces between polar molecules in solution and the ionic mineral surface. An electric double layer is caused by the interaction of the negative carbonate groups on the calcite surface and positively charged solution molecules. This is shown schematically in Figure 1. This phenomenon limits physical adsorption at the calcite surface to organic molecules which produce a positive field.

Chemical adsorption--. In chemical adsorption, a true compound is formed between surface ions and adsorbate molecules. Sharing of electrons, as well as donation of electrons, characterizes the type of bond and the interacting sites. The stability of chemisorbed compounds in aqueous solution depends upon the solubility product of the newly formed compound and commonly upon the pH of the solution, if organic compounds with dissociable acid groups are involved (see Table I).

Competitive adsorption--. Both compounds, solvent and solute, may be adsorbed on the carbonate surface. The polarity of the water molecule causes strong competitive adsorption with the polar solute molecule on the mineral surface. Therefore, the relative strength of the dipole moment of organic molecules with respect to water is significant in determining the extent of sorption for each organic compound on the carbonate surface.

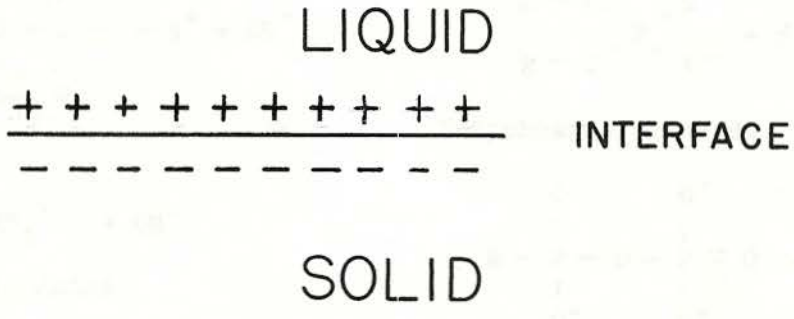


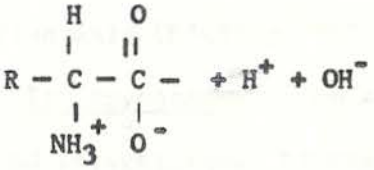
Figure 1. Electric double layer on the surface of calcite immersed into a liquid phase.

In a solid-liquid system, with calcite as suspended phase, positively charged molecules are adsorbed in the form of an immobile layer on the calcite surface. One possible explanation for this phenomenon is that the small positive calcium ions are drawn inward and the large negative carbonate groups outward. This would result in a net negative surface charge of calcite.

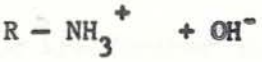
Table I. Structural formulas of some ionic organic compounds which are known to associate with mineral surfaces.

After Ekwall, et al., 1965, Smith and Bader, 1961, and Brooks et al., 1950

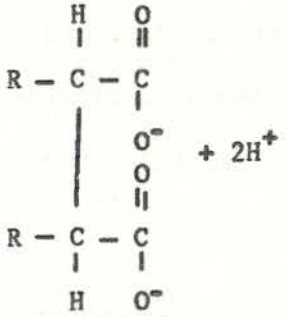
Amino Acids



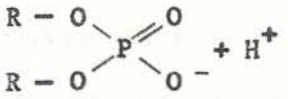
Amines



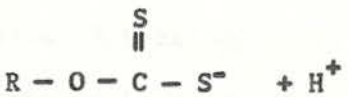
Carboxylic Acids



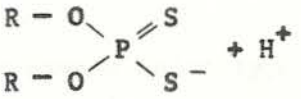
Di(organic)phosphoric Acids



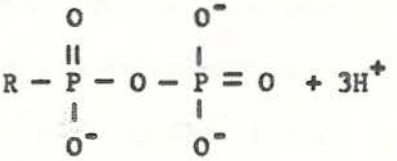
Xantanes



Dithiophosphates

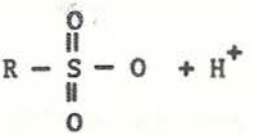


Polyphosphoric Acids

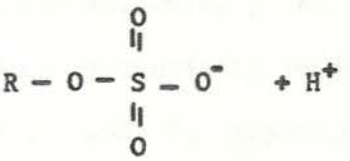


Mercaptans

Sulphonates



Organic Sulfates



Organic compounds with a dipole moment smaller than that of water might be expected to adsorb only in insignificant amounts; whereas, compounds with dipole moments larger than that of water are more likely to interact.

Competitive adsorption may be recognized by the S-shape of an adsorption isotherm (as defined on page 18) which is convex towards the concentration axis (Kipling, 1965, p. 179-180).

Ion exchange--. Ion exchange is the second major type of solid-liquid interaction. If the liquid is an ionic solution and the solid has exchangeable ion sites, such interactions might be expected. The processes are further subdivided into cation and anion exchange, according to the sign of the electrical charge of the exchangeable ions.

Ion exchange is to be expected in the proposed organic carbonate interactions, considering the ionic surface of calcium carbonate and the structure of organic molecules according to Table I.

Conclusion

From the review of natural and artificial systems describing organo-mineral associations and from conceptual and experimental treatment of such associations in surface chemistry, the following points are relevant to this study. Organic compounds which can potentially interact with the surface of carbonate minerals are shown in Table I. Important characteristics of these compounds are their reactive groups, their ionization constants in water, and the strength of their dipole moments.

One may hypothesize that the interaction between carbonate minerals and dissolved organic compounds is a function of the net surface charge. Thus, in the case of calcite, which has a negative surface charge, one would anticipate that organic molecules with a positive field would associate significantly.

The mechanism of association (called sorption) may be physical adsorption, chemical adsorption, or ion exchange. The polarity of water as the universal solvent suggests that adsorption of water is strongly preferred over organic molecules during the experimental study.

The interacting sites of the organic molecules and the carbonate surface can be identified by infrared spectroscopy.

An experimental approach toward study of organo-carbonate associations requires carefully controlled conditions in the specific adsorption system; temperature, pH, and concentrations of the interacting species must be monitored.

II. MODEL EXPERIMENTS ON ORGANO-CARBONATE ASSOCIATIONS

Introduction

Associations of carbonate minerals with stearic acid, alanine, and albumin are measured and interpreted. The experimental conditions are intended to model, but not necessarily duplicate, naturally occurring examples of carbonate surface coating. In this way it is possible to gain information on the association mechanism, to exemplify quantitative treatment of such phenomena, to establish and interpret some model systems.

In accordance with surface chemistry terminology, the organic compounds investigated are called adsorbates. The various carbonate minerals represent the adsorbents, and water and hexane are the solvents in all of the experimental systems considered. Presentation of the interaction data is in the form of an adsorption isotherm, which is a graphic representation of the adsorption of dissolved organic compounds per unit area of mineral surface as a function of concentration. The mineral surface and its associated organic compounds reach equilibrium after a period of time and under constant temperature conditions. Figure 2 is an example of an adsorption isotherm from the system calcite-stearic acid-benzene after data from Suito et al., 1955.

Adsorbates--. The adsorbates include fatty acids, amino acids, and proteins. Stearic acid is one of the classical compounds used in

Figure 2

(a) Four different isotherms describe the adsorption of stearic acid by calcite powders of different shapes and grain sizes. The mean diameter and specific surface areas of the four calcite powders are:

Calcite Sample	Diameter Micron	Specific Surface m^2 per gram
A	1.5	1.52
B	1.8	1.33
C	3.0	0.75
D	0.069	32.39

Scale change: The axes of high concentration and large amounts adsorbed refer to calcite sample D.

(b) All four isotherms fall very nearly on the same curve if the amounts adsorbed are plotted as milligrams per cm^2 vs. the concentration in moles per cm^2. This indicates that, regardless of size and shape of the calcite particles, only the surface interacts with stearic acid. Furthermore, it suggests that the mechanism and type of association are the same in all four experiments.

The data are from Suito et al., 1955, Bull. Inst. Chem. Res., Kyoto Univ., 33, #1 and #8.

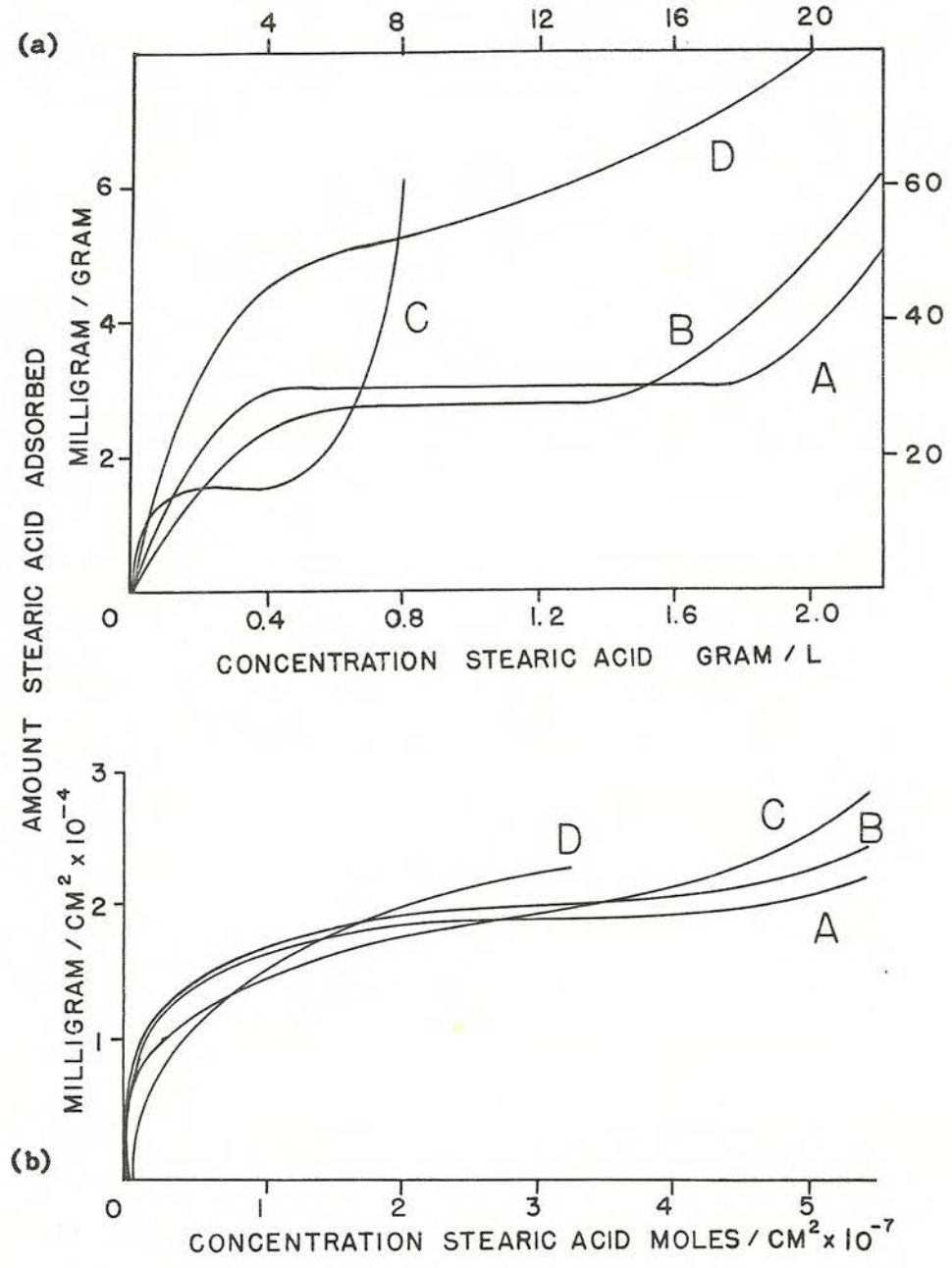


Figure 2. Adsorption of stearic acid by calcite as a function of the surface area.

the study of interfacial phenomena (Küster, 1894; Langmuir, 1917; Freundlich, 1926; Kipling, 1965). Its surface-active properties and molecular dimensions are well known from many hundreds of investigated systems containing stearic acid as an adsorbate. Stearic acid is found dissolved in seawater (Table IX).

D,L-alanine, a simple aliphatic amino acid, was chosen because of its high isoelectric point, pI = 6.107, and because of its high second ionization constant, $pK_2 = 9.866$. These properties lead to low hydrogen ion concentrations when the acid is dissolved in water which allows experiments to be performed without dissolving the solid.

Albumin was found to be surface active (Arnold and Pak, 1962; Shinoda et al., 1963; Joly, 1965) and to demonstrate variable ionic properties at different pH values.

Adsorbents--. Calcite and dolomite are the two most important rock-forming carbonate minerals. Calcite is the rhombohedral form of $CaCO_3$. Dolomite, $CaMg(CO_3)_2$, is an ordered rhombohedral calcium-magnesium carbonate containing equal amounts of each of the two cations. Alternate basal planes of the crystal lattice are occupied either by calcium or by magnesium.

Aragonite and a spectrum of magnesium calcites are the dominant biogenic carbonate minerals (Chave, 1954a, 1954b, 1962). Aragonite is the orthorhombic polymorph of $CaCO_3$. Its main producers in the marine environment are coelenterata, mollusks, and green algae.

Magnesium-calcites are rhombohedral calcium magnesium carbonates that are secreted mainly by calcareous sponges, brachiopods,

Table II. Properties of adsorbates, adsorbents, and solvents.

Adsorbates	Formula	Molecular Weight	Molecular Dimensions	
Stearic Acid	$CH_3(CH_2)_{16}COOH$	284	Length:	23.0 Å
			Diameter:	5.1 Å
			Area, perpendicular	20.5 $Å^2$
			Area, parallel	100 $Å^2$
Alanine	$CH_3CH(NH_2)COOH$	90		
Albumin		69000	Length:	150 Å
			Diameter:	40 Å
			Area, at pH=2	0.89 m^2/mg
			at pH=5	0.58 "
			at pH=7	1.13 "

Adsorbents	Formula	Crystal System	Specific Surface Area
Calcite	$CaCO_3$	Rhombohedral	0.714 m^2 per gram
Dolomite	$CaMg(CO_3)_2$	Rhombohedral	0.743 "
Mg-calcite	$(Ca_{0.89})^{Mg}{}_{(0.11)}CO_3$	Rhombohedral	1.176 "
Aragonite	$CaCO_3$	Orthorhombic	0.8 * "

* Estimated from microscopic examination; for specific surface area determination of other carbonate minerals see Appendix I.

Solvents		Dipole Moment
Water	polar	1.82 mu
Hexane	non-polar	0

red algae, echinoderms, bryozoans, and benthic forams. A compositionally defined member of this spectrum is referred to as Mg-calcite$_{(X)}$, where (X) is the mole fraction Mg / (Ca + Mg) in the structure (Land, 1967).

Solvents--. Water and hexane are the solvents in the investigated systems and were selected for their polar and non-polar properties.

Experimental adsorption

The adsorption of stearic acid from hexane and water solutions and of albumin from aqueous solution by various carbonate minerals is illustrated in isotherms. The investigated systems are in Table III.

Table III. Experimental systems of organo-carbonate interactions

Adsorbent	Adsorbate	Solvent
Calcite	Stearic Acid	Hexane
Dolomite	Stearic Acid	Hexane
Calcite	Stearic Acid	Water
Dolomite	Stearic Acid	Water
Aragonite	Stearic Acid	Water
Mg-calcite	Stearic Acid	Water
Carbonates	Alanine	Water
Calcite	Albumin	Water
Aragonite	Albumin	Water
Mg-calcite	Albumin	Water
Dolomite	Albumin	Water

Properties of adsorbents--. Natural calcite was obtained from vein fillings in limestone of the Ordovician Jacksonburg Formation in Eastern Pennsylvania. Chemical analysis showed 1.5 mole per cent total cations other than calcium. Dolomite was obtained from a dolomitized

reef of Niagaran age from Indiana. Less than 1% cations were found other than calcium and magnesium. Aragonite was collected from Oculina sp., a Bermuda reef coral, and Mg-calcite$_{(0.11)}$ from the echinoderm, Mellita sp. The skeletal samples were chloroxed and all carbonate samples hand ground with mortar and pestle and passed through a 34 micron screen. The powders were kept in a desiccator and at no time prior to the experiments were they in contact with any liquid substance.

Specific surface area determinations were performed in cooperation with the Department of Chemistry, Lehigh University, after the method of Brunauer, Emmett, and Teller using argon gas. The experimental results are given in Appendix I and are summarized in Table II.

Microscopic examination of the powdered carbonates showed well-defined cleavage rhombohedra of calcite and dolomite; whereas, the Oculina and Mellita fragments were irregular. The Mellita sp. fragments are bound by concave planes resulting from the typical arrangement of pores in all echinoderm skeletons. This characteristic shape accounts for a specific surface area, at equal overall diameter, larger than that of the smooth calcite and dolomite rhombs.

Carbonate mineral - stearic acid - water systems--. C^{14}-labelled stearic acid in aqueous solutions was prepared and the concentration determined by liquid scintillation counting. Preweighed amounts of powdered carbonate minerals were added to the stearic acid solution of known concentration. The samples were intermittently shaken and allowed to equilibrate with the atmosphere. After 24-30 hours, when the mineral particles had settled, the final concentration of stearic acid was determined and the specific adsorption calculated. For detailed

description, calibration curves, and results, see Appendix II.

Carbonate - stearic acid - hexane system--. Experiments in the hexane system were carried out principally as described above. However, there was a basic difference in that the initial concentration of stearic acid in hexane was kept constant and increasing amounts of calcite and dolomite were added.

The suspensions were centrifuged and aliquots of supernatant withdrawn for liquid scintillation counting. There was no difference in adsorption with different times ranging from three minutes to several hours. Figure 5 shows C^{14}-stearic acid coated calcite.

Carbonate minerals - amino acid - water system--. Dilute solutions of D,L-alanine were prepared and the pH adjusted with NaOH to 8.90, 9.86, and 10.50. Calcite, dolomite, aragonite, and Mg-calcite$_{(0.11)}$ were each added to a series of samples, then stirred and centrifuged.

Carbonate minerals - albumin - water system--. Purified egg albumin was dissolved in distilled water, dissolution hastened by addition of KOH. Eight samples of successively lower concentrations were prepared by dilution for each system.

To the albumin solution were added constant weights of powdered calcite, Mg-calcite$_{(0.11)}$, aragonite, and dolomite. The system was investigated at pH 7 and pH 10. One series of experiments of the pH 10 system equilibrated for 3 days, and a second series for 3 weeks. Blanks, standards, and calibration curves were determined spectrophotometrically on ninhydrin assays (Clark, 1964). See Appendix II for detailed description, calibration curves, and results.

Experimental Results

Carbonates - Stearic acid - Hexane system

Shape and description of isotherms--. The isotherms in Figure 3 describe the adsorption of stearic acid by calcite and dolomite. In the calcite - stearic acid - hexane system, there is strong initial adsorption at low concentrations. As concentration increases, adsorption gradually approaches a first limiting value of 6×10^{-6} moles/g of calcite. A slight but marked decrease in specific adsorption is observed with a minimum at approximately 6×10^{-5} moles stearic acid per liter hexane. At still greater concentration, stearic acid is again very strongly adsorbed as shown by a continued rise of the isotherm. Adsorption does not seem to reach an ultimate limiting value. The isotherm was obtained through two independent series of experiments. The first series covers a wide concentration range from $0.2 - 6.5 \times 10^{-5}$ moles per liter and is marked by +. The second series, describing adsorption at very low concentrations, is marked by •.

In the dolomite - stearic acid - hexane system, limiting adsorption is approached at a value of only 2.6×10^{-6} moles per gram, about ½ of the specific adsorption of stearic acid by calcite. Again, the isotherm shows a minimum at approximately 6×10^{-5} moles per liter, after which there is a strong increase in specific adsorption without approaching an ultimate limiting value.

The shapes of both isotherms up to the first limiting value may be fitted by the following equation:

Figure 3

The maximum adsorption of stearic acid by calcite is about twice that of dolomite, i.e., 6×10^{-5} moles and 2.6×10^{-5} moles stearic acid per gram of solid. Calcite has twice as many calcium surface sites as dolomite. Both isotherms show a minimum of adsorption at 6×10^{-5} moles stearic acid per liter of hexane. This concentration corresponds to the monomer-dimer equilibrium of stearic acid in benzene according to Maryott et al. (1949).

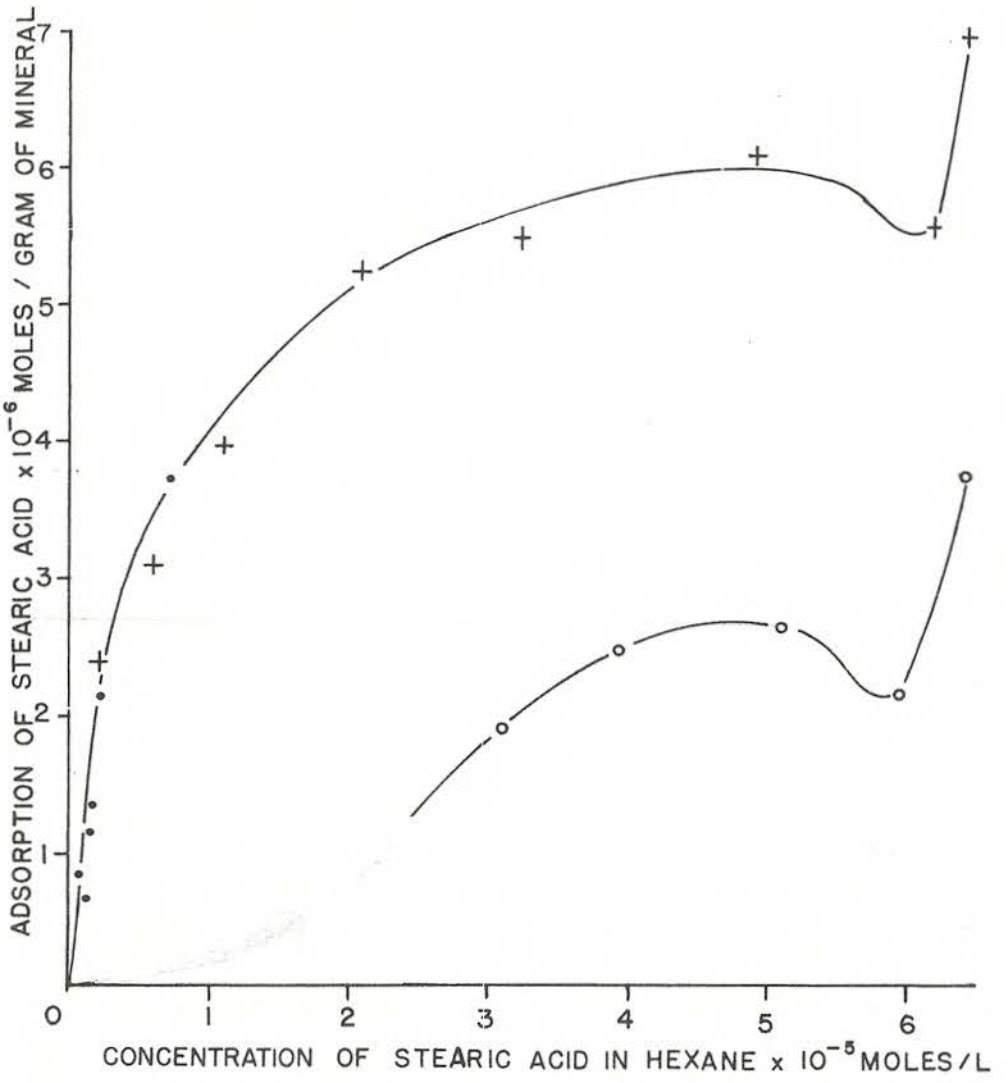


Figure 3. Adsorption of stearic acid by calcite and dolomite from hexane solution.

(1) $$\frac{x}{m} = K \times C^{\frac{1}{n}}$$

$\frac{x}{m}$ = amount adsorbed per gram of solid

C = final concentration of stearic acid in hexane

K = constant

n = constant

This expression is known as the Freundlich equation and was derived empirically (Kipling, 1965, p.24). A plot of the experimental results in the form of the Freundlich equation is in Figure 4. Adsorption at very low concentration does not fit this equation; however, all experimental points at high concentrations do fit well.

For justified usage of the Freundlich equation in solid-liquid systems, Kipling (1965) presents a derivation, applicable to dilute solutions only, based on changes of the surface free energy of the solid before and after adsorption. The amount adsorbed corresponds to a fraction of the solid surface covered with adsorbate. At the limiting value, this amount represents a complete monolayer of adsorbate.

The experimental results suggest that stearic acid associates with the calcium sites of calcite and dolomite. This implies that there is a complete monolayer formation at the surface of calcite and a 50% monolayer coverage of the dolomite surface.

Monolayer formation at the limiting value of adsorption can be checked independently by comparing the mineral surface areas available for coverage to the actual area covered by stearic acid molecules. Such a comparison requires assumptions of molecular area and arrangement of adsorbate molecules at the mineral surface.

Figure 4

The experimental points of Figure 3 are plotted in the form of the Freundlich equation:

$$\frac{x}{m} = K \times C^{\frac{1}{n}}$$

$\frac{x}{m}$ = amount adsorbed

C = final concentration

K = slope

$\frac{1}{n}$ = intercept

Adsorption is well described by the Freundlich equation at high concentrations, but at low concentrations this function is not adequate. From the intercept, n is calculated for determining the reduction in the surface free energy of calcite by adsorption of stearic acid. For these calculations, see pages 60-61. Only the specific adsorption at high concentrations is of importance to this calculation; therefore, the inadequacy of the Freundlich equation at low concentrations can be neglected.

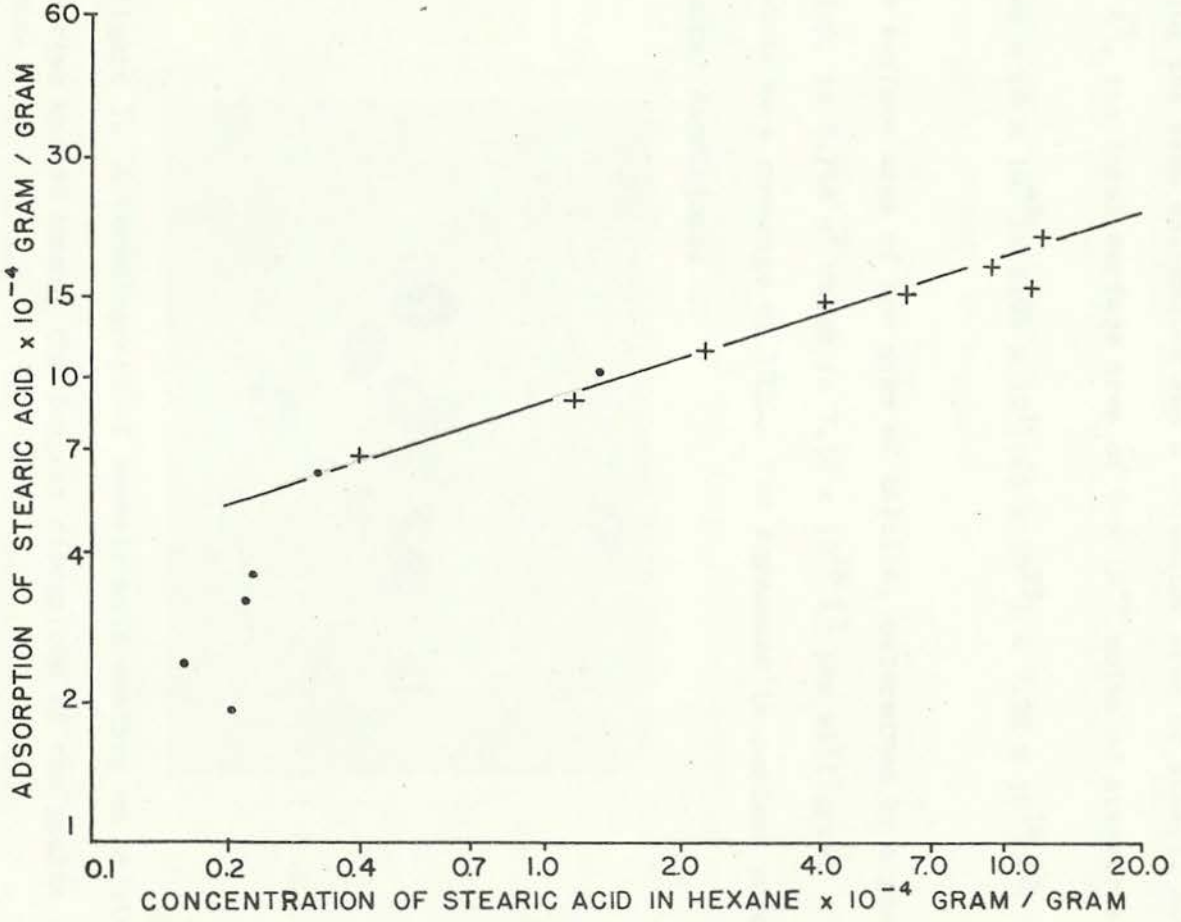


Figure 4. Adsorption of stearic acid by calcite

Suito et al., (1955) demonstrated that stearic acid molecules are closely packed on the calcite surface with their long axes perpendicular to the mineral surface.

Using the same assumption and a molecular area of stearic acid of 20.5 $\mathring{A}^2$, the total surface area of 6×10^{-9} moles of stearic acid is:

$$\text{Area} = (6 \times 10^{-9}) \times (2.05 \times 10^{1}) \times (6 \times 10^{23}) = 7.38 \times 10^{16}\ \mathring{A}^2$$

The surface area of one gram of calcite, determined by argon adsorption, is 0.714 m^2 which is 7.14×10^{16} $\mathring{A}^2$ per milligram. This corresponds to a coverage of 103%. The agreement is perfect under the experimental conditions.

Figure 5. Autoradiograph of stearic acid coating on calcite. Exposure time was 60 hours, the longest dimensions of the grains are 50 microns.

For dolomite, the specific surface area is 7.43×10^{16} per mg; the limiting value of adsorption is 2.6×10^{-9} moles per mg. This is equal to 3.2×10^{16} $\mathring{A}^2$, and thus represents a 43% coverage of dolomite surface by stearic acid.

The minimum adsorption shown by both isotherms is apparently caused by a change in effective concentration (activity) of the adsorbate molecules and not by the surface of the minerals. According to the experimental determination, this minimum exists at a solution concentration of $10^{-4.23}$ moles per liter. A.A. Maryott et al. (1949) report $10^{-4.23}$ moles per liter as the equilibrium concentration for monomer-dimer formation of stearic acid in benzene. Since both hexane and benzene are non-polar solvents, it is reasonable to assume that the minima in specific adsorption are caused by decrease in concentration of stearic acid monomers. Specific adsorption at high concentrations may increase because of beginning multilayer formation of dimeric molecules on the initial layer. This, however, is only one possible explanation.

Structure of adsorbed layer--. The differential coverage of calcite and of dolomite (103% vs. 43%) by stearic acid in hexane solution clearly suggests a structural influence of the crystal lattice upon the adsorption.

Since both minerals are present as cleavage rhombohedra, it is reasonable to assume that the structure of the cleavage surface is reflected in the adsorbed layer. The cleavage surface of calcite and of dolomite have interplanar spacings of 6.41 Å and 6.18 Å, respectively, enclosing angles of 101°55' and 102°57'. Four cations are on each corner and one in the center of the faces. The area of a face of the calcite unit cell is 40.4 $\mathring{A}^2$ per 2 $CaCO_3$, and that of the dolomite unit

Figure 6

The stearic acid molecules are adsorbed with the carboxyl end on the calcite surface. The small circle in the center of the stearic acid molecule is a carbon atom (diameter = 2.22 Å) and the two large circles are oxygen atoms (diameter = 2.45 Å). The total area occupied by one stearic acid molecule is 20.5 $Å^2$. Dimensions and configuration of the stearic acid molecule are from Deamer and Cornwell, 1966, Biochim. Biophys. Acta, 116, 555-562.

The lattice dimensions of calcite are A = 6.42 Å and B = 102°. The outlines show a face of the calcite unit cell; its area is 40.4 $Å^2$.

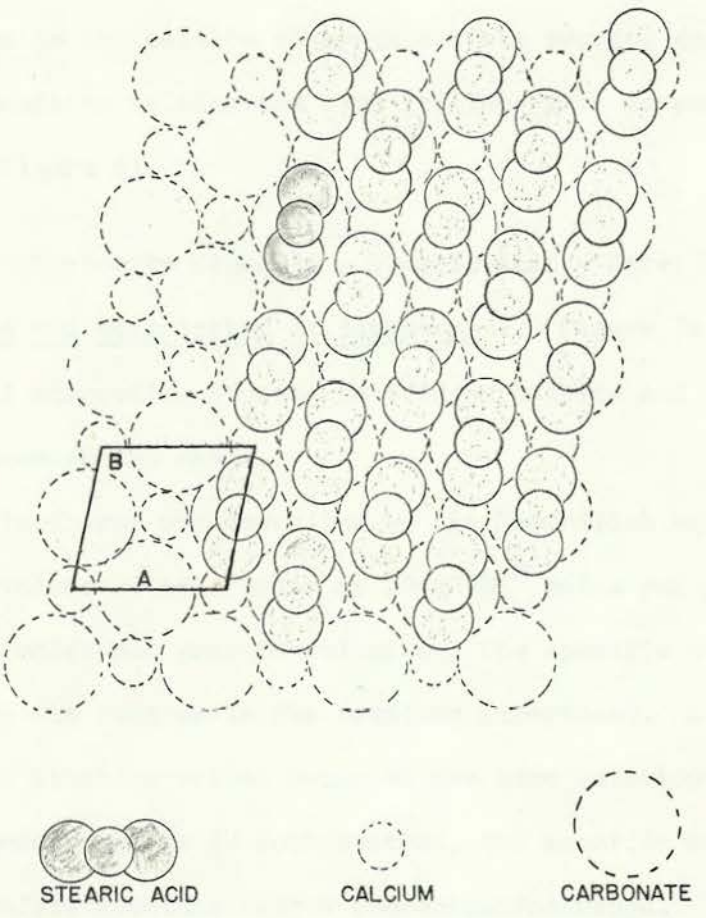


Figure 6. Proposed structure of stearic acid monolayer superimposed onto the calcite lattice.

cell is 37.4 $Å^2$ per $CaMg(CO_3)_2$. The calcium concentration at the dolomite surface is ½ that at the calcite surface. The spacing of the calcium sites on the calcite cleavage surface permits exactly one stearic acid molecule to be adsorbed with its long axis perpendicular to the surface (Figure 6).

Carbonate Minerals - Stearic Acid - Water Systems

Shape and description of isotherms--. Figure 7a illustrates isothermal adsorption of stearic acid by calcite and dolomite over a large concentration range.

The isotherms are described by the Freundlich equation up to their limiting values of adsorption at 20×10^{-8} moles per gram of calcite and 12×10^{-8} moles per gram of dolomite. The specific surface area of the solids are the same as in the previous experiment. As in hexane solution, both limiting values occur at the same solution concentration. At higher concentrations in both systems, the specific adsorption increases up to fivefold within a narrow concentration range. The initial parts of the isotherms, up to the limiting values, differ in specific adsorption of calcite and dolomite. The specific adsorption of dolomite is 60% that of calcite.

Beyond the sharp increase of specific adsorption, both systems become indistinguishable. They tend towards an upper concentration limit of about 25×10^{-8} moles stearic acid per liter water.

In the second series of experiments (Figure 7b), the ratio of adsorption of calcite to adsorption of dolomite is also 1:0.5. The specific adsorptions of aragonite, Mg-$calcite_{(0.11)}$, and calcite are identical, at least at the lower end of the concentration range.

Figure 7a

The adsorption isotherm of the system calcite-stearic acid-water is marked by +, that of the system dolomite-stearic acid-water by o. Both isotherms approach a limiting value of adsorption at a solution concentration of about 20×10^{-8} moles of stearic acid per liter of water. The specific adsorption of calcite is about twice that of dolomite. Note the duplicate determinations at 14×10^{-8} moles of dissolved stearic acid and 18×10^{-8} moles of adsorbed stearic acid in the calcite system, and at 12×10^{-8} moles of adsorbed stearic acid and 17×10^{-8} moles of dissolved stearic acid in the dolomite system.

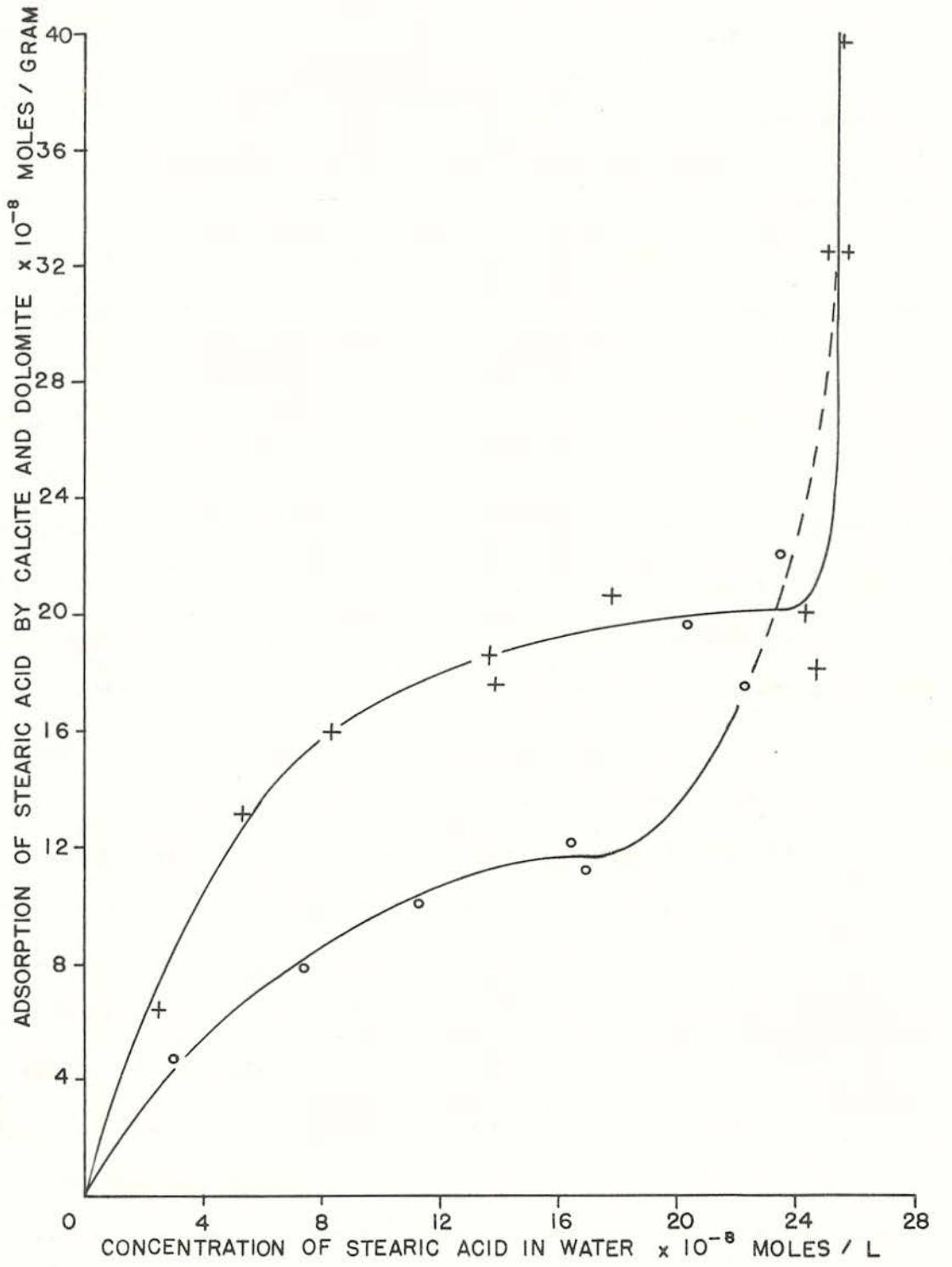


Figure 7a. Adsorption of stearic acid by calcite and dolomite from aqueous solution.

The nature of adsorbed layer--. The total areas represented by 20×10^{-8} moles and 12×10^{-8} moles of stearic acid are 2.4×10^{18} $Å^2$ and 1.44×10^{18} $Å^2$, respectively, according to the formula:

(2) Total Area = Moles x Avagadro number x Molecular area

However, comparison between the available calcite and dolomite surface areas per gram of solid and the actual area covered by adsorbed stearic acid indicates that only 3.6% and 1.9% of the respective solid surfaces are covered.

If the orientation of the long axes of the stearic acid molecules is parallel to the mineral surface, coverage improves to 18.5% of the calcite and 10.5% of the dolomite surface. It needs to be pointed out here that the approximate coverage of 1/5 and 1/10 of the mineral surfaces is not the maximum coverage as indicated by the three to five-fold increase of specific adsorption at high solution concentrations in Figure 7a.

From the ratio of specific adsorption of calcite to dolomite, it may be concluded that the surface concentration of calcium sites determines the nature of the adsorbed layer. The concentrations of calcium on the surfaces of calcite and dolomite are 8.25×10^{-6} moles Ca^{++} per m^2 and 4.45×10^{-6} moles Ca^{++} per m^2, respectively.

The surface concentration of adsorbed stearic acid at the limiting value of these two minerals is 2.7×10^{-7} moles per m^2 and 1.2×10^{-7} moles per m^2. Therefore, stearic acid is associated with 3.3% of the calcium sites of the calcite and with 3.6% of the calcium sites on the dolomite surface.

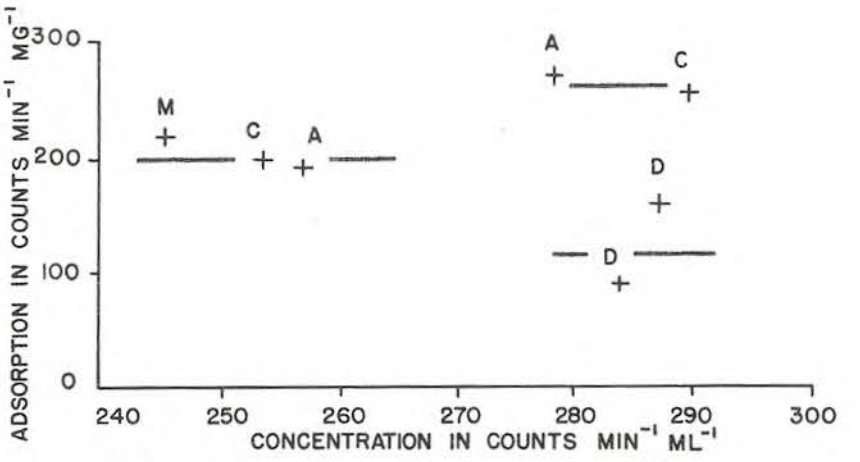


Figure 7b. Adsorption of stearic acid by various carbonate minerals.

In these adsorption systems no complete isotherms were determined. Adsorption of single samples of aragonite (A), Mg-calcite (M), calcite (C), and dolomite (D) were measured. Concentration of stearic acid in water and adsorption of stearic acid per milligram of solid are given in counts per minute per milliliter of solution, rather than in moles of stearic acid or any other absolute concentration units. Note the similarity of calcite and aragonite adsorption, the slightly higher adsorption of Mg-calcite$_{(0.11)}$, and the low dolomite adsorption.

Water appreciably expands the layer and, therefore, causes a larger coverage. Incorporation of other ions in the adsorbed layer has the same effect. Bicarbonate and hydroxyl ions may form a stearate complex of large specific surface area, thus achieving complete coverage of the mineral surface. This latter possibility is proposed for the investigated system.

Calcium - stearate complex formation--. A different kind of association dominates at high concentrations as indicated by the sudden increase of specific adsorption. This association may be spontaneous multilayer formation. However, the very steep slope of the isotherm at high concentrations suggests a second interpretation. If a reaction takes place between the surface ions of the mineral and the adsorbate molecules, and if these interacting ions and molecules are also present in the solvent, the same reaction may occur as precipitation from solution. Precipitation would be indicated by a sudden increase of apparent adsorption. In this case, it can be visualized that at concentrations below 25×10^{-8} moles of stearic acid per liter, a compound is formed through reaction of surface ions and adsorbed molecules; whereas, above 25×10^{-8} moles per liter, this same compound is formed by precipitation from solution (Garrels, 1968, personal communication).

The following ionic and dissolved molecular species may interact in the system after isothermal adsorption has come to a steady state and equilibrium is reached with atmospheric P_{CO_2}:

(3) Ca^{++}, HCO_3^-, $CO_3^{=}$, $StAc^o$, H^+, OH^-

Mg^{++} can be excluded from participating in a possible reaction because it is only present in one system. The stearic acid concentration is known. Calcium is determined by EDTA titration, and the HCO_3^- and $CO_3^=$ concentrations (≈ activities) are calculated from pH measurements. It is assumed that the solution equilibrated with either atmospheric P_{CO_2} or the carbonate solids.

Ion products have been calculated for ten possible reactions. Atmospheric P_{CO_2} is assumed for five reactions; these are marked in Table IV by *. For two hypothetical reactions, equilibration is assumed with the carbonate solids (calcite or dolomite); these are marked by #. No carbonate species participate in the remaining three reactions.

It is evident from the calculations that equilibrium with atmospheric P_{CO_2} is the better assumption, especially since the reaction vessels were open to the atmosphere. (For detailed explanation, see facing page of Table IV.). Because of slow equilibration, the true bicarbonate concentration lies between the two assumptions. Only three of the calculated reactions will be discussed here.

Formation of calcium stearate --. The formation of calcium stearate from solution gives consistent ion activity products averaging 22.98 (Column g, Table IV); however, they do not agree with the thermodynamic value of 19.6 (du Ritz, 1965, Irani and Callis, 1960). Calcium stearate was not formed at the mineral surface because the ion activity product is not constant.

Calcium stearate complexes --. The ion activity products which best fit the total data and match the two analogous experiments in the calcite and dolomite adsorption systems are:

Table IV

The ion activity products in each column are calculated from the analytical values of experiments shown in Figure 7a. The first column always shows the ion activity product from the calcite-stearic acid-water system; whereas, the second column refers to the dolomite-stearic acid-water system. Hypothetical associations marked by * contain ion activities of the carbonate species calculated from the pH, assuming equilibrium with atmospheric P_{CO_2}. Those values marked by # contain activities of carbonate species calculated from the metal ion concentration, assuming equilibrium with calcite or dolomite in the respective experimental system.

It is evident from Columns a, b, c, d, i, j, o, p, s, and t that equilibrium with atmospheric P_{CO_2} is a better assumption than equilibrium with the carbonate solids because the ion activity products are more consistent.

Table IV. Ion activity products of hypothetical calcium-stearate associations.

$pCa+pHCO_3+pStAc$*		$pCa+pHCO_3+pStAc+pH$*		$pCa+pOH+pStAc$		$pCa+2pStAc$		$pCa+pCO_3$*		
a	b	c	d	e	f	g	h	i	j	
15.60	16.37	24.58	24.84	18.23	19.00	22.84	23.09	7.29	8.58	surface reaction
15.65	15.67	24.69	24.84	18.28	18.30	23.10	23.12	7.13	7.15	
15.60	15.72	24.64	24.90	18.23	18.35	22.99	23.22	7.14	7.17	
15.66	15.67	24.71	24.87	18.29	18.30	23.20	23.28	7.05	6.99	
15.97	16.36	24.72	24.96	18.60	18.99	23.22	23.36	7.55	8.29	
16.03	16.18	25.04	25.21	18.66	18.81	23.75	23.92	7.26	7.37	
15.90	16.07	24.89	25.22	18.53	18.70	23.52	23.84	7.25	7.31	
15.98	16.66	25.10	25.29	18.61	19.29	23.98	24.04	6.99	8.21	
16.28	16.19	25.03	25.31	18.91	18.80	23.86	24.06	7.57	7.25	
16.60	16.67	25.43	25.75	19.23	19.30	24.63	24.88	7.34	7.39	
16.46	-	24.76	-	19.09	-	22.98	-	8.87	-	ppt
16.22	-	24.69	-	19.16	-	22.91	-	8.46	-	
16.15	-	24.66	-	18.78	-	22.89	-	8.34	-	
16.06	-	24.66	-	18.69	-	22.92	-	8.13	-	

$pCa+pHCO_3+pStAc$#		$pCa+pSt+pH$		$pCa+pOH+pStAc+pHCO_3$*		$2pCa+pStAc+pH+pCO_3$#		$2pCa+pStAc+pH+pCO_3$*		
k	l	m	n	o	p	q	r	s	t	
25.69	26.80	22.19	21.94	20.62	21.90	30.59	32.48	29.84	30.52	surface reaction
25.96	28.32	22.36	22.64	20.61	20.50	30.76	33.18	29.49	29.79	
25.90	28.33	22.31	22.71	20.56	20.54	30.71	33.29	29.45	29.88	
26.06	28.33	22.39	22.70	20.61	20.47	30.79	33.15	29.44	29.69	
25.47	27.25	22.10	22.19	20.22	21.76	30.50	32.77	29.65	30.48	
26.20	28.35	22.68	22.87	21.02	21.15	31.08	33.38	29.94	30.24	
26.08	28.58	22.51	23.00	20.91	20.92	30.91	33.59	29.76	30.31	
26.59	27.64	22.85	22.55	20.86	22.03	31.25	33.11	29.84	30.76	
25.80	28.26	22.41	23.06	21.53	21.05	30.81	33.63	29.98	30.31	
26.33	28.92	22.89	23.46	21.77	21.59	31.29	34.02	30.33	30.85	
24.29	-	21.69	-	22.16	-	30.09	-	30.56	-	ppt
24.63	-	21.79	-	22.06	-	30.19	-	30.25	-	
24.72	-	21.80	-	21.64	-	30.20	-	30.14	-	
24.93	-	21.89	-	21.46	-	30.29	-	30.12	-	

(4) $$pK_a = pCa^{++} + pHCO_3^- + pStAc^o$$

(5) $$pK_b = pCa^{++} + pOH^- + PStAc^o$$

Neither is more probable than the other because pOH^- and $pHCO_3^-$ are both calculated from the same pH values.

The variability of ion activity products within a series of experiments is due to the deviation of the actual activity of CO_2 in solution from the assumed value of $10^{-4.97}$. The agreement between analogous experiments in both systems with unknown, but presumably identical, internal CO_2 activity is considered significant in evaluating a possible reaction. (See Columns a,b,e,f in Table IV). Two hypothetical reactions may describe the formation of the calcium stearate - bicarbonate complex at the mineral surface and the formation of this precipitate from solution

(6) surface reaction:
$$CaCO_3 + StH \leftrightarrow Ca(HCO_3)St$$

(7) Precipitation from solution:
$$Ca^{++} + HCO_3^- + StH \leftrightarrow Ca(HCO_3)St + H^+$$

Discussion

Both types of complex metal soaps have been reported. Thomas and Schulmann have shown that $Me(OH)St$- and $Me(HCO_3)St$ -complexes form condensed solid films on an aqueous subphase (1954), Me^+ = metal.

Polyvalent metal ions that form complex soaps are Al^{+++}, Cr^{+++}, Fe^{++}, and Cu^{++}. Bagg et al., (1964) reported the composition of stearic acid monolayers on calcium-containing substrates. They found no evidence for (HCO_3^-), (PO_4^{3-}), or (NH_3^+) complexes in the calcium stearate layer using infrared analysis. However, Deamer, Meek, and

Cornwell (1967) found a Mg-stearate complex with (OH^-) absorption bands in addition to H_2O. They also reported water in calcium stearate monolayers.

There is a significant difference between the monolayers investigated by these workers and the carbonate mineral-stearic acid association proposed here. Monolayers, spread on an aqueous substrate containing metal ions in solution, have different structural requirements than are imposed by a crystal lattice upon the adsorbed layer at the solid-liquid interface. Therefore, it is possible that they also deviate in composition, and that the proposed complexes are a valid interpretation for carbonate mineral-stearic acid interactions.

Thomas and Schulmann (1954) found a marked increase of surface area per Me-stearate complex. For Cu(OH)St and $Cu(HCO_3)St$, they report 28 $\AA^2$ per molecule and 41 $\AA^2$ per molecule, respectively, at pH 6.4. If this increase is taken into consideration, the calcite and dolomite surface area is completely covered. Table V summarizes the composition and the orientation of possible calcium stearate complexes.

Carbonate minerals-amino acid-water systems

None of the investigated carbonate minerals, calcite, dolomite, aragonite, and $Mg\text{-}calcite_{(0.11)}$ adsorbed any dissolved alanine.

The concentration changes expected were estimated to be well within the precision of the method used. The pH of the systems was varied so that the dominant alanine species were either negatively or positively charged. At the isoelectric point, an equal concentration of positive and negative sites can interact with the carbonate surface. The ionic species at different pH values are illustrated in Figure 8.

Table V. Composition and orientation of possible stearic acid carbonate associations and estimated coverage of the mineral surface.

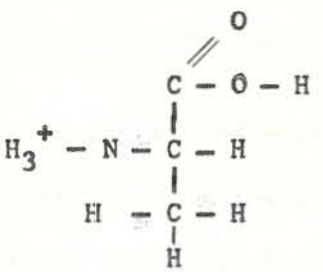
Orientation of molecules	Composition of layer	Coverage	
Long axes perpendicular to mineral surface	$CH_3(CH_2)_{16}COOH$	3.6%	1.9%
Long axes parallel to the mineral surface	$CH_3(CH_2)_{16}COOH$	18.5%	10.0%
Long axes parallel, layer hydrated	$CH_3(CH_2)_{16}COOH \cdot nH_2O$	>18.5%	>10.0%
Calcium-bicarbonate-stearate complex	$Ca(HCO_3)CH_3(CH_2)_{16}COO$	10%	5%
Calcium-bicarbonate-stearate complex, hydrated	$Ca(HCO_3)CH_3(CH_2)_{16}COO \cdot n\,H_2O$	* 100%	+ 50%

* Proposed for the calcite surface
\+ Proposed for the dolomite surface

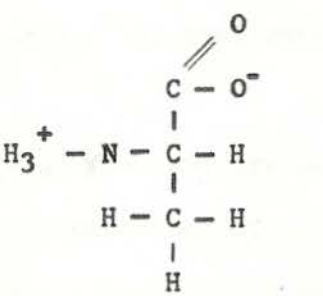
The first column under coverage refers to the calcite surface, the second column to the dolomite surface. Per cent coverage, assuming perpendicular orientation of the adsorbed stearic acid molecules, was calculated using a specific coverage of one stearic acid molecule of 20.5 Å^2. At parallel orientation of the long axes, the specific coverage was assumed to be 100 Å^2.

The increase in per cent of coverage, assuming hydrated stearic acid molecules, can only be given as greater than 18.5% and greater than 10.5%. The specific surface area of a calcium-bicarbonate-stearic acid molecule is taken as that reported for a copper-bicarbonate-stearic acid complex by Thomas and Schulman (1954). A hydrated calcium-bicarbonate-stearic acid complex with its long axis parallel to the mineral surface gives the largest possible coverage.

D,L-Alanine below pH = 2.348 = pK_1



D,L-Alanine at pH = 6.107 = pI



D,L-Alanine above pH = 9.866 = pK_2

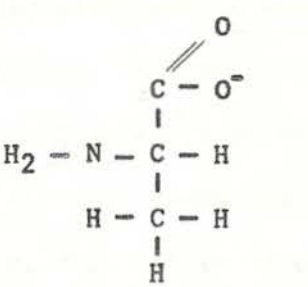


Figure 8. Ionic species of dissolved alanine at different pH.

At the isoelectric pH the overall charge of an alanine molecule is zero. Below pH = 2.348, all molecular species are positively charged; and above pH = 9.866, all species are negatively charged. The presence of these differently charged species allows testing experimentally for ion-exchange phenomena between alanine and calcite.

It seems from the negative outcome of the experiment that simple ion exchange reactions do not take place between the ionic organic species, such as alanine, and the carbonate surface.

Carbonate minerals-albumin-water systems

Three isotherms were determined in the system containing purified albumin as adsorbate (Figures 9 and 10). Two of these describe pH effects. The third isotherm was obtained from a long term (three weeks) experiment using aragonite as adsorbent. The adsorption of albumin by Mg-calcite$_{(0.11)}$ and by dolomite was qualitatively tested with four samples.

Calcite-albumin-water--. The isotherm obtained at pH 7 shows no adsorption at albumin concentrations of up to 23 mg per liter. Perhaps this is due to preferred adsorption of water (competitive adsorption) on the mineral surface. Above a concentration of 23 mg per liter, a sudden increase of specific adsorption occurs which instantaneously reaches a limiting value of 0.69 mg/gram. This value is very likely maintained over a large concentration range before it decreases (see Fig. 9B). The same system at pH 10 shows the same initial preferred adsorption of water (see Fig. 9A). Above albumin concentration of 11 mg per liter, there is the same sudden increase of adsorption as noted in isotherm B. Adosrption reaches a limiting value of 0.77 mg/gram over a slightly larger concentration range than in the low pH system. At increasingly higher concentrations the specific adsorption of albumin by calcite increases steadily. Between a solution concentration of 55 and 61 mg per liter, the specific adsorption abruptly drops to zero from a maximum of 2.3 mg per gram.

Figure 9

The calcite-albumin-water system was investigated at pH 7 (B) and pH 10 (A). In both systems the isotherms approach about the same limiting value of adsorption of 0.7 milligram of albumin per gram of calcite. No adsorption takes place at concentrations smaller than 10 milligrams and 23 milligrams of albumin per liter of water in the respective systems. At concentrations larger than 30 mg per liter, the shapes of the isotherms are not clearly determined; however, a pronounced drop in adsorption was consistently encountered in all experiments using albumin as adsorbate.

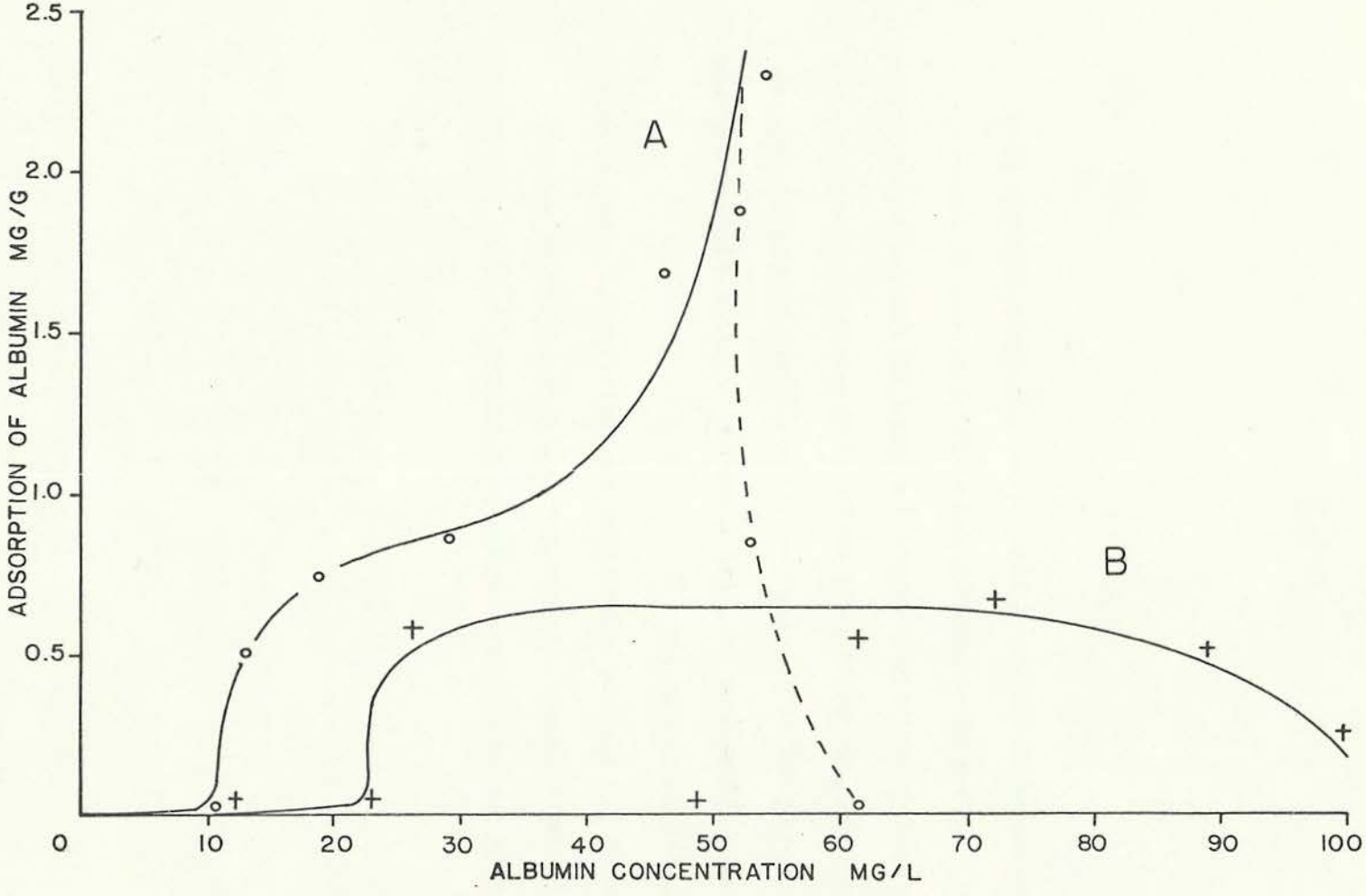


Figure 9. Adsorption of albumin by calcite from aqueous solution.

Figure 10

The adsorption isotherm of the system aragonite-albumin-water shows a limiting value of adsorption near 0.5 milligram of albumin per gram of aragonite and a pronounced increase of adsorption at higher concentrations (i.e., 25 milligrams to 35 milligrams of albumin per liter of water). At 40 milligrams per liter an abrupt drop of adsorption takes place. This drop has been observed in other albumin systems as well, but cannot be explained.

Mg-calcite (M) adsorbs albumin to essentially the same extent as aragonite (A) under identical conditions. Adsorption of albumin by calcite over a period of three weeks is indicated by (C).

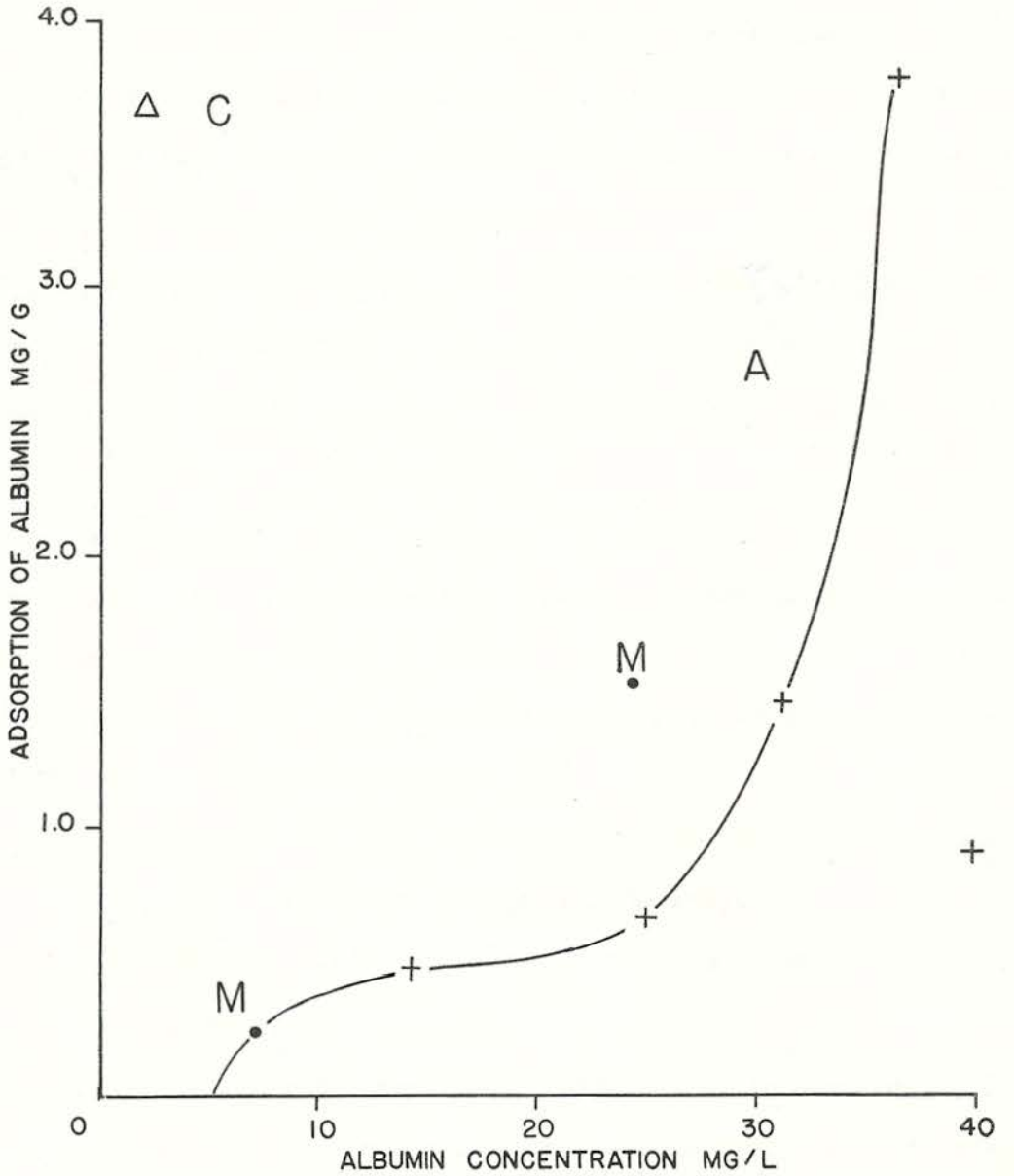


Figure 10. Adsorption of albumin by aragonite, Mg-calcite, and calcite.

Aragonite-albumin-water--. The lack of experimental points makes it difficult to give a detailed description of the long term adsorption isotherm obtained from aragonite (Figure 10). The general shape, however, is similar to the calcite-albumin-water isotherm of Figure 9A. Specific adsorption approaches a limiting value of 0.53 mg per gram which is followed by a threefold increase. Again, there is an abrupt drop of adsorption after this maximum.

Mg-carbonates-albumin-water--. There was no concentration change in the albumin solution after powdered dolomite was added. This lack of adsorption existed for three weeks of exposure of the dolomite surface to the solution.

However, an amount of albumin significantly higher than that adsorbed by calcite or aragonite at the same solution concentration was adsorbed by Mg-calcite$_{(0.11)}$.

In general, an adsorption isotherm in the carbonate-albumin-water system has the following characteristics:

1) At low adsorbate concentrations, isotherms are strongly convex towards the concentration axis.
2) Limiting values of adsorption are observed at intermediate concentrations.
3) At high concentrations, there is a minimum of adsorption which may or may not be preceded by an increase of adsorption several times greater than the limiting value.
4) This maximum seems to be time and pH dependent.

Competitive adsorption--. There appears to be strong preferential adsorption of water at low albumin concentrations in the three systems investigated. This is indicated by the convex shape of the isotherm towards the concentration axis. It appears that the preferred adsorption of water is influenced by the pH of system. (See Figure 9, isotherms A and B.) The system at pH 10 shows competitive adsorption up to 11 mg albumin per liter, and at pH 7 up to 23 mg per liter. Above the isoelectric point of albumin (pI = 4.8), the concentration of negatively charged albumin species increases. Therefore, the adsorption system of pH = 10 has more negatively charged albumin species than the system of pH = 7. It may be inferred that these albumin species compete effectively with the water molecules for the carbonate surface.

Nature of adsorbed layer--. The limiting value of adsorption at intermediate concentrations is almost the same for the systems at pH 10 and pH 7. The respective values are 0.77 mg/g and 0.69 mg/g. Assuming an area of 1.13 m^2/mg albumin, spread as a monolayer over an aqueous substrate of pH 7.4 (Arnold and Pak, 1962), the specific adsorption at the limiting value may be interpreted to indicate complete coverage of the carbonate surfaces.

The agreement between the surface area of adsorbed albumin and that of the carbonate mineral adsorbents in Table VI might be deceptive because the specific surface area of albumin varies strongly depending on the pH of the aqueous subphase. At pH 2.2 the surface area of 1 mg of albumin is 0.89 m^2. At pH 5.1 (near pI), it is 0.58 m^2 and at pH 7.4, 1.13 m^2 (Arnold and Pak, 1962).

Table VI. Coverage of the mineral surface by adsorption of albumin in the system $CaCO_3$-albumin-water.

Adsorption system	Specific adsorption mg/gram	Surface area of adsorbed albumin m^2/gram	Specific surface area of mineral m^2/gram
Calcite-albumin-water at pH 7	0.69	0.78	0.714
Calcite-albumin-water at pH 10	0.77	0.87	0.714
Aragonite-albumin-water, long term	0.53	0.60	0.8 *

* estimated from microscopic examination

The specific adsorption values are taken from Figure 9 and 10; they represent the limiting values of adsorption of each system. The surface area of adsorbed albumin per gram of solid is calculated from data given by Arnold and Pak (1962). These data represent the surface area of one milligram of albumin spread on the surface of water at different pH values.

The specific surface area of the minerals was determined by argon adsorption. (For detailed procedure see Appendix I. Note the agreement between Columns 3 and 4.)

Multilayer formation and related processes--. Multilayers of albumin may form on carbonate minerals in systems with high pH values and over long periods of time. One calcite sample adsorbed more than ten times the amount required to form a monolayer, almost depleting the solution of albumin (indicated by C in Figure 10). This might be the result of an aggregation process of albumin on carbonate grains. This process forms particles which consist of more protein than carbonate mineral.

The abrupt drop of adsorption after the maximum and the well-documented minimum of adsorption at high concentrations cannot be explained. Perhaps denaturation processes of albumin account for this phenomenon. Multivalent ions cause denaturation. For example, copper nitrate in albumin solution causes formation of aggregates which do not precipitate (Sarahoff and Choate, 1954). These aggregates might not be adsorbed by the carbonate surfaces because of reduction of surface-active sites.

Principal experimental conclusions

Adsorption in the carbonate-stearic acid-hexane system is characterized by isotherms which approach a first limiting value of adsorption. A complete monolayer of stearic acid is indicated on calcite; the dolomite surface appears to be only 50% covered. The crystal lattice dimensions of calcite and dolomite and the surface concentration of calcium on both minerals impose rigid geometric requirements on the structure of the adsorbed layer. A chain-like structure of the stearic acid layer may be proposed for both mineral surfaces.

The isotherms for the carbonate-stearic acid-water systems show the same ratio of calcite to dolomite adsorption as do those in the system containing hexane as solvent. However, the limiting values do

not correspond to complete and half coverage of the respective mineral surfaces unless hydration and/or complex formation is assumed. Only 3.6% of the calcite and 1.9% of the dolomite surface would be covered with pure stearic acid, assuming that the long axes of the molecules are oriented perpendicularly to the mineral surface.

It appears that calcium stearate complexes are produced. They are calcium-bicarbonate soap and calcium-hydroxy soap:

(8) $Ca(HCO_3)St \cdot n H_2O$

(9) $Ca(OH)St \cdot n H_2O$

Positive, negative, and neutral ionic species of alanine are not measurably adsorbed by any of the investigated carbonate minerals.

Strong preferred adsorption of H_2O over albumin is indicated at low albumin concentrations in the carbonate-albumin-water systems. The competition seems pH dependent, and possibly reflects the ratio of negatively charged protein molecules to neutral species.

The minerals are completely covered by a film of albumin at intermediate concentrations. The film may, with time, act as a center for further aggregation of protein.

Effects on Carbonate Equilibration

The foregoing experiments suggest four ways in which organic compounds may influence carbonate-solution interaction.

Physical isolation of the reactive mineral surface through aggregation of organic compounds is one reaction inhibiting effect. Reduction in surface free energy by a monolayer reduces the carbonate solubility. Solubility products of newly-formed surface complexes are different from

those of the bulk solid, so that the solution is in an "apparent" saturation state with respect to the bulk solid. Differential solution of Mg-carbonates may be caused through preferred adsorption of stearic acid by calcium.

Physical isolation

Dissolved organic compounds aggregate around nucleii of carbonate particles in the form of thick impermeable coatings. This aggregation may occur spontaneously or may follow formation of an initial monolayer. The thick coating does not necessarily have a defined structure, but may include an appreciable amount of solvent or even colloidal-sized particles of different origin. Inhibition of chemical interaction is caused by physical isolation of the carbonate particles from the surrounding solution. Chave (1965b), Wangersky and Gordon (1965), and Chave and Suess (1967) reported natural aggregates of this type containing carbonate mineral particles. Chave (1965a) suggested that these aggregates inhibit chemical interaction.

Reduction in surface free energy

The surface free energy is a thermodynamic expression of the reactivity of a solid surface. It is the sum of the specific surface free energy of the substance plus the contribution from edges, corners, and dislocations. The latter contributions are only significant at small grain sizes where the concentration of edges and corners per unit area is considerably greater. This effect on the reactivity of solids is known as the Small Particle Solubility Effect (SPSE) (Pantin, 1965; Weyl, 1958).

The surface energy of a calcite cleavage rhombohedral face is 230 ergs per cm^2 (Gilman, 1960). Chave and Schmalz (1966) have shown that SPSE becomes noticeable between a grain size of 10^{-4} and 2×10^{-5} cm, The total energy of the surface increases to 300 ergs per cm^2. They measured this effect in terms of equilibrium pH and expressed it as increased activity of $CaCO_3$. They also showed that the surface energy of much larger particles can be raised tremendously through grinding. When the calcite crystal surface is completely coated by a monolayer, the surface free energy is reduced (Pantin, 1965).

It is possible to calculate the reduction in surface free energy when the covering constitutes a complete monolayer. The relationship between the Freundlich equation (empirical) and an expression used by Henry (1922) (thermodynamic) indicates the reduction in surface free energy ΔS is:

(10) $$S_o - S_1 = R \times T \times \left(\frac{x}{m}\right)_m \times n$$

(11) Freundlich equation:

$$\frac{x}{m} = K \times C^{\frac{1}{n}}$$

(12) Or, in logarithmic form:

$$\ln \frac{x}{m} = \ln K + \frac{1}{n} \ln C$$

(13) Henry's equation:

$$\ln \frac{x}{m} = \frac{R \times T \times \left(\frac{x}{m}\right)_m}{S_o - S_1} \times \ln C + \ln K$$

(14) It follows from equations (12) and (13) that:

$$\frac{1}{n} = \frac{R \times T \times \left(\frac{x}{m}\right)_m}{S_o - S_1}$$

S_o = Surface free energy of calcite particles in contact with pure solvent, mean diameter of particles = 10^{-4} cm, S_o = 230 ergs/cm^2

S_1 = Surface free energy at monolayer formation

$(\frac{x}{m})_m$ = Amount adsorbed at monolayer formation = $7.83 \cdot 10^{-10}$ moles cm^{-2}

R = Gas constant = $8.314 \cdot 10^7$ ergs $mole^{-1}$ $degree^{-1}$

T = Temperature of experiment in degrees Kelv. = 300°

$\frac{1}{n}$ = Slope of $\log \frac{x}{m}$ vs. log C, graphically obtained from Figure 4 = 0.313

C,K,n as defined in Figure 4

(15) $$0.313 = \frac{8.314 \cdot 10^7 \cdot 3.0 \cdot 10^2 \cdot 7.83 \cdot 10^{-10}}{S_o - S_1}$$

$$S_o S_1 = \frac{19.45}{0.313} = 62 \text{ ergs } cm^{-2}$$

For particles of 10^{-4} cm in diameter, the surface free energy drops from 230 ergs per cm^2 to 168 ergs per cm^2 through adsorption of a stearic acid monolayer. There is as yet no quantitative relation established between surface free energy and equilibrium pH of calcite in solution. It can be expected that the activity coefficient of a coated calcite particle is smaller than unity.

Solubility of surface complexes

The Ca^{++} and $CO_3^{=}$ concentrations (= activities) of the solution in contact with the proposed surface complex of $Ca(HCO_3)St$ gives ion activity products for $CaCO_3$ ranging from 8.50 to 7.00 (see Table IV, Column i). The solubility product of calcite $pK_{calc.}$ = 8.40. The mean ion activity product of pCa + pCO_3 is 7.3 for those samples which showed surface reaction. This indicates that the solution is not in equilibrium with calcite.

Surface complexes that contain calcium influence the ratio of

magnesium to calcium dissolving from Ca-Mg-carbonates because the complexes will not affect the magnesium concentration. Calcium to magnesium ratios vary from 1.93 - 0.85 in the ten dolomite samples from which the adsorption isotherm was established (Figure 7a). There is indication that the larger ratios coincide with increasing coverage by surface complexes. The accuracy of the cation determination does not allow positive correlation with the high coverage. Therefore, these results are not definitive. To clarify this, small amounts of dolomite were dissolved in large volumes of aqueous stearic acid solution, and calcium and magnesium were accurately measured. Table VII shows a ratio of calcium to magnesium of 65 to 35 when the solid to solution ratios are smaller than 2. Presumably, the dolomite rhombs were more completely covered by surface complexes at these ratios. At solid to solution ratios greater than 2, dolomite dissolved congruently--perhaps because coverage by surface complexes was less complete than at lower ratios. The "apparently" incongruent dissolution of calcium from dolomite and its implication to natural waters is not understood.

Table VII. Dissolved calcium and magnesium from a suspension of dolomite in an aqueous stearic acid solution.

Ratio of solid to solution	Cations moles per liter Ca^{++}	$(Ca^{++}+Mg^{++})$	Per cent Ca^{++}	Per cent Mg^{++}
0.1	3.23×10^{-4}	4.75×10^{-4}	68	32
0.3	2.50	3.77	67	33
0.5	1.67	2.71	62	38
0.7	1.67	2.73	63	37
0.9	1.58	2.48	64	36
1.2	1.13	1.67	68	32
1.6	1.42	2.22	64	36
2.0	1.05	1.95	55	45
12.5	0.46	0.98	47	53
20.0	0.37	0.72	51	49

Selective coating

If the calcium sites on a magnesium-carbonate surface are only partly covered by adsorbed organic molecules, the solubility of magnesium might increase due to the relative increase of magnesium-carbonate surface which is free from stearic acid. A multicomponent equilibrium exists between organic-calcium complexes on part of the surface and the remaining complex-free mineral surface. Such a situation seems to be present in a system containing Mg-calcite$_{(0.13)}$, stearic acid, and water.

Table VIII. Dissolved calcium and magnesium from a suspension of Mg-calcite$_{(0.13)}$ in an aqueous stearic acid solution.

Ratio of solid to solution	Cations moles per liter Ca^{++}	$(Ca^{++} + Mg^{++})$	Per cent Ca^{++}	Per cent Mg^{++}
0.1	2.60×10^{-4}	4.53×10^{-4}	58 ± 3%	42 ± 3%
0.3	2.35	3.29	71	29
0.5	2.42	3.40	71	29
0.7	2.30	2.84	81	19
1.2	3.45	4.25	81	19
1.6	3.38	3.65	92	8
2.0	1.93	2.10	92	8
5.0	1.68	2.03	83	17
12.5	1.86	2.22	84	16
20.0	1.81	2.28	80	20

Table VIII summarizes the calcium and magnesium distribution in an aqueous stearic acid solution in contact with Mg-calcite$_{(0.13)}$.

At solid to solution ratios smaller than 1.0, magnesium is preferentially dissolved; above 1.0 there is essentially congruent dissolution of Mg-calcite$_{(0.13)}$. This differential dissolution may be attributed to differential coverage of the mineral surface by calcium stearate complexes.

III. SORPTION OF NATURAL SURFACE-ACTIVE COMPOUNDS FROM SEAWATER

Organic Matter in the Sea

The organic matter in seawater is arbitrarily subdivided into particulate and dissolved portions based on filtration, centrifugation, and other methods of separation. (For other characteristics, see Duursma, 1965.) Riley (1963) has suggested that a dynamic equilibrium exists between the dissolved organic content of seawater and the particulate fraction. He proposed inorganic adsorption as the controlling mechanism.

Dissolved Compounds

Duursma (1965) summarized the literature on dissolved organic constituents detected in seawater. Surface-active compounds listed in this summary include fatty acids, proteins, lipids, fatty alcohols, and unspecified polypeptides.

Fatty acids--. Fatty acids range in concentration from 0.1-0.8 mg per liter and show little variation with depth in the sea. These concentrations are between three and four orders of magnitude larger than those at which the adsorption experiments were carried out (see Chapter II). The dissolved fatty acid fraction is therefore sufficient to form complete surface coatings on suspended carbonate particles.

Many workers refer to part of the fatty acid fraction in seawater as free fatty acids. It would be of interest to clarify the state of dissolved fatty acids in the presence of approximately 0.01 moles of calcium and 0.06 moles magnesium per liter of seawater. Other dissolved cations may also interact with fatty acids. For the purpose of this paper, the term "free fatty acids" is used with the understanding that

the true state of dissolved fatty acids in seawater is not known.

Lipids--. Jeffrey et al. (1964) report a mixture of complex lipids extracted from seawater. Most of these compounds are surface active to a certain extent. Triglycerids, diglycerids, monoglycerids, and phospholipids; saturated and unsaturated hydrocarbons; sterol esters and free sterols occur in varying concentrations. The amount of individual compounds ranges from 5-13 mg per liter. Such high concentrations are perhaps local, and the average value for seawater is one or two orders of magnitude smaller. There is, however, still enough dissolved material to cause significant adsorption onto mineral surfaces.

Fatty alcohols--. The list of natural surface-active compounds in seawater is completed by reports of fatty alcohols. Garrett (1967) has shown the presence of long-chained alcohols, dodecanol and cetyl alcohol.

The presence of so many different groups of surface-active compounds in seawater makes the formation of organo-carbonate associations highly probable. Furthermore, the concentrations indicate that these compounds exist in sufficient quantities to form coatings of one or more layers on any suspended carbonate minerals. Groups and individual compounds with their respective concentrations are in Table IX.

Particulate matter

The study of particulate organic matter concerns two aspects of organo-carbonate associations. First, organic particles from seawater contain carbonate minerals (Chave, 1965; Wangersky and Gordon, 1965;

Johannes, 1967). Secondly, the mechanism of formation is probably based on adsorption phenomena (Riley, 1963).

Adsorption theory--. Baylor, Sutcliffe and Hirschfeld (1962) have shown that organic particles are produced on the surface of bubbles rising through seawater. Riley (1963) suggested a dynamic equilibrium between dissolved compounds and the concentration of particles. MacIntyre (1965) showed a 700-fold increase of phosphorous concentration in the spray of bursting bubbles. Sutcliffe, Baylor, and Menzel (1963) found earlier that bubble-produced organic particles are high in phosphorus and are surface active.

The observations and experiments of these workers, and the experiments described in this study, suggest that similar phenomena exist at the seawater-bubble interface and at the seawater-carbonate interface. The surfaces of suspended minerals provide nucleii for adsorption and aggregation of dissolved surface-active matter.

Living matter theory--. It should be noted here that marine biologists agree on the importance of particulate organic matter as a source of food, but that there is strong disagreement on the mode of formation of these aggregates. The inorganic adsorption theory is opposed by the theory that particulate organic matter is formed by the interaction of living bacteria. Barber (1966) has shown that certain bacterial species cause formation of aggregates; in the absence of these species, no organic aggregates are formed. Sheldon, et al. (1967) also reported that repeated filtration of seawater effectively prevents particle formation i.e., "...particle formation was caused by something that was not removed by normal (nonaseptic) filtration through a 0.22 micron membrane, but

was removed by successive filtration." "Something", other than bacteria which is removed by successive filtration, is dissolved surface-active matter.

Perhaps both inorganic adsorption and bacterial agglutination are important in the formation of organic aggregates. Bacteria may populate and enlarge aggregates which initially are formed by adsorption at the air-water or solid-water interface.

The sea surface

Adsorption at the sea-air interface--. Garrett and Jarvis have described the organic chemical composition of the sea surface and the related changes in the physical properties. They find that the major constituents of surface films are free fatty acids, fatty esters, and fatty alcohols (Garrett, Timmons, Jarvis, and Kagarize, 1963; Garrett, 1967; Jarvis, 1967; Jarvis, Garrett, Scheiman, and Timmons, 1967; and Williams, 1967). An extract of sea surface-active material shows a sharp increase of film pressure at an area of 1.5 m^2 occupied by 1 mg of substance. This indicates close packing of the film constituents. The area is about 1/3 of that occupied by the same amount of stearic acid spread as a close packed film on water. Other properties of natural surface films are damping of capillary waves (Garrett and Bultman, 1963), retardation of evaporation (LaMer, 1962), and effects on surface temperature and convective water motion (Jarvis, Timmons, and Zisman, 1962).

Sutcliffe, Baylor, and Menzel (1963) found soluble phosphorous enrichment in converging oceanic windrows near Bermuda. They reasoned that the vertical sea-surface circulation (Langmuir) concentrates organophosphate surface films.

Table IX. Surface-active compounds in seawater.

Fatty acids	Formulas	* Concentration	Author
Caprylic acid	$CH_3(CH_2)_6COOH$	-	A
Capric acid	$CH_3(CH_2)_8COOH$	-	A
Lauric acid	$CH_3(CH_2)_{10}COOH$	0.01-0.32	B
Myristic acid	$CH_3(CH_2)_{12}COOH$	0.01-0.10	B
Myristoleic acid	$CH_3(CH_2)_3CH{:}CH(CH_2)_7COOH$	-	B
Palmitic acid	$CH_3(CH_2)_{14}COOH$	0.01-0.17	B
Palmitoleic acid	$CH_3(CH_2)_5CH{:}CH(CH_2)_7COOH$	0.02-0.16	B
Stearic acid	$CH_3(CH_2)_{16}COOH$	0.04-0.09	B
Oleic acid	$CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$	0.01-0.02	B
Linoleic acid	$CH_3(CH_2)_4CH{:}CH(CH_2)CH{:}CH(CH_2)_7COOH$	0.01	B
Fatty alcohols	**Formulas**	*** Concentration**	**Author**
Dodecanol	$CH_3(CH_2)_8CH_2OH$	-	A
Cetyl alcohol	$CH_3(CH_2)_{14}CH_2OH$	-	A

Proteins	Composition	* Concentration	Author
Peptides	C:N = 13.8:1	-	C
Polypeptides	-	0.021 surface	D
18 amino		0.014 200 m	D
acids detected		0.006 2000 m	D
		0.006 3120 m	D

Complex lipids +	Dominant constituents	* Concentration	Author
Fraction I	Paraffinic hydrocarbons	0.82-0.95	E
Fraction III	Sterol esters of fatty acids	0.06-0.10	E
Fraction IV	Fatty acids	0.30-2.90	E
Fraction VI	Diglycerids (?)	0.40-2.20	E
Fraction VII	Monoglycerids	0.90-3.00	E
Fraction VIII	Phospholipids and unidentified	0.60-0.80	E

* Concentrations in milligrams per liter

\+ Soluble in ethyl acetate

A Garrett, W. D., 1967, Deep-Sea Res., v.14, pp.221-227.

B Slowey, J. F., L. M. Jeffrey, and D. W. Hood, 1962, Geochim. et Cosmochim. Acta, v.26, pp.607.

C Jeffrey, L. M. and D. W. Hood, 1958, J. Mar. Res., v.17, pp.247.

D Degens, E. T., J. H. Reuter, and K. N. F. Shaw, 1964, Geochim. et Cosmochim. Acta, v.28, pp.45.

E Jeffrey, L. M., B. F. Pasby, B. Stevenson, and D. M. Hood, 1964, in Advances in Organic Geochemistry, Ed. Colombo and Hobson, pp.175-197.

Table X contrasts the dissolved organic carbon concentration of four regular surface water samples with four samples which were skimmed off the surface by a 30-mesh screen--all taken from Kaneohe Bay, Oahu, Hawaii. (For method, see Garrett, 1965.) The pronounced increase of dissolved carbon in the skimmed sample is attributed to organic surface film which forms at the air-sea interface.

Table X. Dissolved organic carbon of regular surface water and uppermost surface layer, Kaneohe Bay, Oahu, Hawaii.

Station #	Surface water mg Carbon/liter	Skimmed surface mg Carbon/liter
1 calm	1.5	8.1
2 calm	2.2	6.25
3 calm	2.2	6.1
4 calm	2.6	6.25
4a slick	2.6	7.7
5 slick	2.1	5.9

Surface-active matter in the atmosphere--. Blanchard (1964) collected air-borne particulate matter along the shores of Hawaii and found that these salt water droplets carried a highly compressed surface-active film. Atmospheric particles of this nature are condensation nucleii for raindrops (Blanchard and Woodcock, 1956). Duce, Woodcock, and Moyers (1967) found that these particles have I/Cl and I/Br ratios which are two to three orders of magnitude larger than those of seawater. They believe that perhaps the organic film mechanism is responsible for the enrichment of iodine.

Adsorption at the air-water interface is well documented by observations and experiments. Experimental adsorption at the solid-seawater interface is described in the following section.

Adsorption of Surface-Active Matter from Seawater by Calcite

Chave and Suess (1967) described an experimental approach toward quantification of organo-carbonate associations. At various ratios of suspended calcite to seawater, there are different stages of organo-carbonate associations. These stages affect the inorganic chemical interaction between calcite and supersaturated seawater. The degree of chemical interaction is measured by pH changes according to the equation:

(16) $$CaCO_3 + H^+ \leftrightharpoons HCO_3^- + Ca^{++}$$

Inorganic precipitation is indicated by a drop of pH.

The results of calcite-seawater reactions are shown in Figure 11 from Chave and Suess (1967). The surface area of 300 mg of fine-grained calcite is entirely coated by surface-active compounds from 200 ml seawater. This occurs very rapidly, before precipitation of $CaCO_3$ can take place. At ratios of 500 or 700 mg of calcite to 200 ml of seawater, adsorption is less effective because of the large surface area of the solid calcium carbonate. With 1000 or 1300 mg per 200 ml, there is essentially uninhibited precipitation as the pH rapidly approaches a steady state. Therefore, waters with different dissolved organic concentrations should show different degrees of inorganic chemical interaction with carbonates. This is tested experimentally by a modified procedure based on the above method.

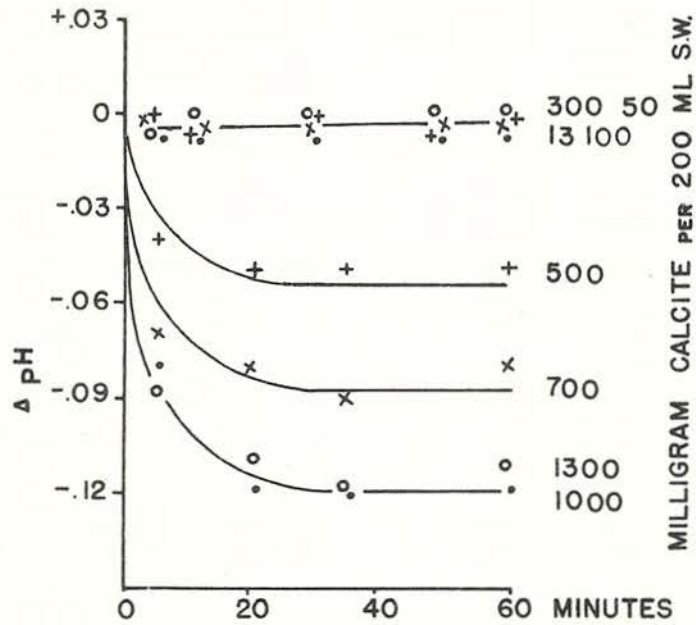
Experimental procedure

Three to five 200-ml samples of seawater from each of four greatly different environments were brought into contact with various amounts of

Figure 11

The numbers on the right indicate the milligrams of calcite powder added to 200 millililiters of seawater. Note that essentially no reaction was recorded when four samples, ranging from 13 to 300 milligrams of calcite, were added; that an intermediate reaction took place when 500 and 700 milligrams were added; and that the maximum reaction occurred when 1000 and 1300 milligrams were added.

This figure is from Chave and Suess, 1967, Suspended minerals in seawater, Trans. N. Y. Acad. Science, Ser. II, v. 29,pp. 991-1000.



$$CaCO_3 + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$$

Saturometry

finely ground calcite. The samples were stirred continuously and the pH monitored over a period of one hour.

In two cases, the seawater consisted of surface samples collected near Bermuda and from the Long Island Sound off New York. The third sample was deep water from 2600 meters off the Bermuda platform. Sample 4 was interstitial water which had been squeezed from a shallow water (1-2 feet) carbonate sediment from Bermuda. The sediment contained about 20% coarse sand-size fragments of Cymopolia sp., an aragonitic green alga. The remainder was mixed carbonate mud. All samples were initially supersaturated with respect to calcite. The results are shown in Figure 12, and a detailed experimental description is in Appendix III.

This modified saturometry method approaching equilibrium from undersaturation was also applied to surface and deep water Bermuda samples.

Results

Observations--. The deep-water sample showed no pH change with time when amounts of calcite smaller than 10 mg were added. Addition of 12 mg, however, produced a slight drop of pH indicating precipitation of $CaCO_3$ on some of the introduced calcite nucleii. When 33 milligrams of calcite were added to the seawater, there was a drop of 0.05 pH units. Larger amounts did not significantly change the final pH. The Bermuda surface water sample behaved in the same general way, except for the much larger amounts of ground calcite (greater than 45 mg) which were necessary to induce inorganic precipitation. The sample from Long Island Sound required still more calcite (greater than 80 mg) before a significant change in pH was observed. Between 90 and 100 mg calcite was added

Figure 12

Ground calcite powder reacts with supersaturated seawater collected from a depth of 2600 meters at a solid-to-water ratio of 7 milligrams per 200 millliliters (A). Surface water from the same area shows beginning inorganic equilibration with calcite at a ratio of 50 milligrams per 200 millliliters (B). Surface water from Long Island Sound begins to equilibrate at a ratio of 70 milligrams per 200 millliliters (C); whereas, interstitial water water from a carbonate sediment does not interact before a ratio of 90 milligrams to 200 milliliter is reached (D). The calcite powder used in these experiments had the same specific surface area, therefore the ratio of solid to seawater represents a ratio of calcite surface area to seawater. When this surface area-to-seawater ratio of a particular seawater sample is reached, the concentration of surface-active compounds is reduced so much that uninhibited inorganic equilibration between calcite and seawater can take place. As long as these ratios are not exceeded, equilibration is inhibited.

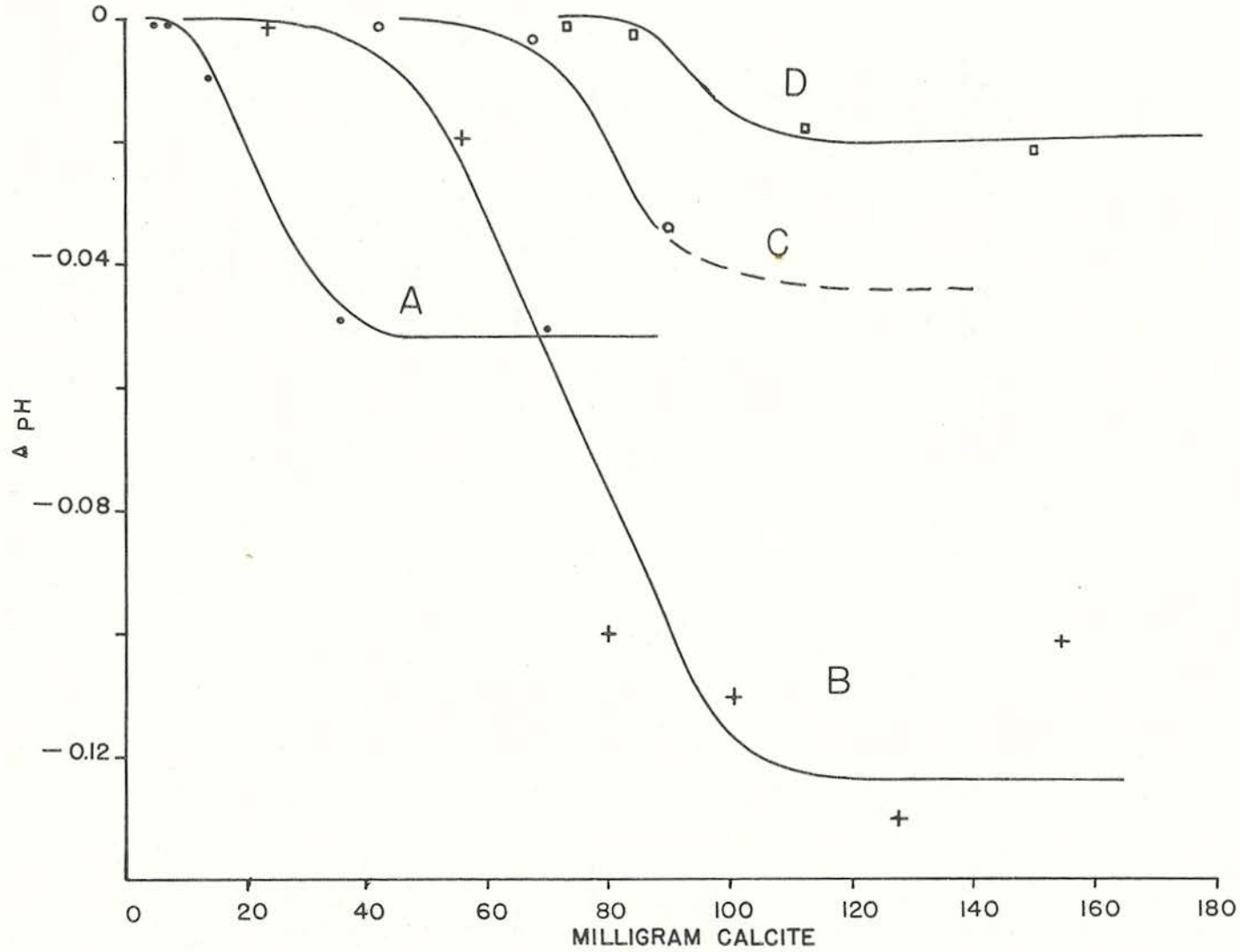


Figure 12. Reactions of calcite with seawater at various solid-to-water ratios.

to the slightly supersaturated interstitial water sample before precipitation was induced.

The Ca^{++} and Mg^{++} concentrations of the samples varied slightly as indicated in Table XI. The variation did not, however, influence the calcium carbonate equilibration in the experiments. Carbonate alkalinity was not determined, but the pH indicates that the surface water samples were of normal marine alkalinity. The deep water and interstitial water samples have alkalinities corresponding to a higher P_{CO_2}.

Table XI. Analyses of sea water used for adsorption experiments.

Water sample		Cation concentrations			
		Calcium		Magnesium	
	pH	moles/liter	ppm	moles/liter	ppm
Deep water	7.90*	0.0110	439 ±4	0.0553	1354 ±10
Surface water	8.26	0.0112	448	0.0588	1430
Interstitial water	7.70	0.0165	464	0.0633	1535

* Surface pH

Interpretation--. For each water sample there is a characteristic amount of calcite required to induce inorganic reaction (Figure 12). For carbonate contents of less than the characteristic amount, the reactive calcite surface is completely coated and inorganic equilibration is inhibited. For values greater than the critical amount, equilibration is approached from super- and undersaturation.

These critical amounts seem to be directly related to the concentration of surface-active compounds in each environment. To confirm that dissolved organic compounds are being removed from seawater by the surface of suspended carbonate minerals, the total dissolved carbon content was monitored.

There is a consistent difference in the amounts of dissolved carbon in seawater before and after exposure to carbonate particles in the two experiments summarized in Table XII.

Table XII. Removal of dissolved organic carbon from seawater by adsorption on calcite.

Water from Kaneohe Bay, Oahu	Total dissolved carbon in milligrams per liter: Regular surface water	Screen-sampled surface water
Before adsorption		
Method a	1.75	8.85
Method b	1.34	-
After adsorption		
Method a	1.57	7.67
Method b	1.19	-
Per cent removed		
Method a	10.0%	13.5%
Method b	11.2%	-

In Method "a", phosphoric acid was used to remove dissolved CO_2; in Method "b", hydrochloric acid was used.

The regular surface water was collected from Kaneohe Bay, Oahu, Hawaii. Depending on the oxidizing agent used in the analyses, the total dissolved carbon content before adsorption was 1.75 mg or 1.34 mg carbon per liter. The dissolved carbon concentration dropped to 1.57 and 1.19 mg per liter, respectively, after exposure to suspended calcite particles for ten to twelve hours. This drop represented an uptake of 10% of the total dissolved organic matter.

An organic-rich film was collected with a screen at Kaneohe Bay. About one gram of reagent-grade calcite powder was added to 100 ml water and stirred for 30 minutes. The dissolved carbon content before addition of the solid carbonate was 8.85 mg per liter; after adsorption, it was 7.76 mg per liter. Therefore, the uptake of dissolved organic matter was 13.5%. The results in Table XII are mean values of triplicate determinations with error of less than 3%.

The surface water sampled by screening had relatively more dissolved surface-active matter than the regular surface water. This difference is presumably shown by the increased uptake of total dissolved carbon by calcite from the screen-sampled water as compared to the regular surface water. Whether or not adsorption is time dependent cannot be determined from these experiments. But the uptake of 13.5% of the total dissolved organic matter in less than an hour's time definitely indicates that adsorption is a fast process. This is also observed in other seawater carbonate interactions.

Characterization of Natural Organo-Carbonate Associations

Other methods used to characterize the natural organo-carbonate associations are histochemical staining techniques, biochemical assaying, and analyses of elemental concentrations of phosphorus.

Staining techniques--. One liter of filtered seawater was stirred with 20 mg of suspended ground calcite for five to six hours. The mineral grains were recovered by filtration, and then stained in 0.1% Methylene Blue at pH 9. The basic dye, Methylene Blue, was chosen because staining at pH values greater than 8.5 protects the calcite grains from dissolution. Freshly-ground calcite powder does not react with Methylene Blue in the described staining procedure.

Microscopic examination shows that the introduced surfaces collect organic matter. In some cases, individual grains are entirely surrounded with a coating of variable thickness. In others, whole clusters of grains are enclosed in larger particles of brownish organic matter. There are also aggregates which are not in contact with carbonate surfaces, as well as grains of carbonates which have no visible coating.

All carbonate mineral phases collect organic matter from seawater. Dolomite, calcite, aragonite, and Mg-calcite$_{(0.11)}$ were used. Figs. 13+14 show stained organic aggregates, clusters, and individually coated grains which were all artificially produced from filtered seawater by suspended calcite.

Biochemical assays--. Biochemical assays were attempted to further characterize the compounds which form organo-carbonate associations. The residue from dissolving the calcite, which had been used for collecting organic matter from solution in seawater, was hydrolized with H_2SO_4. The hydrolysate showed a positive ninhydrin reaction, but subsequent paper chromatography failed to clearly separate any free amino acids. Because of the low protein concentration in seawater and of the possibility of hydrolizing living bacteria, a biochemical characterization of the compounds using the above method is not very promising. A better approach is gas-liquid chromatography of methylated fatty acids, free or in the form of esters. This should be used in further studies.

Elemental analyses--. Sutcliffe, Baylor, and Menzel (1963), as well as MacIntyre (1966), demonstrated the highly significant phosphorus concentration at the air-water interface. Brooks et al. (1950) have shown that phosphorus in the form of polymethaphosphates and polyphosphates (tradename, Calgon) is adsorbed from solution by suspended calcite. Duce, Woodcock, and Moyers (1967) believe that organic films could enrich iodine in atmospheric particles over the sea. Therefore, phosphorus and halogens may characterize the proposed organo-carbonate associations.

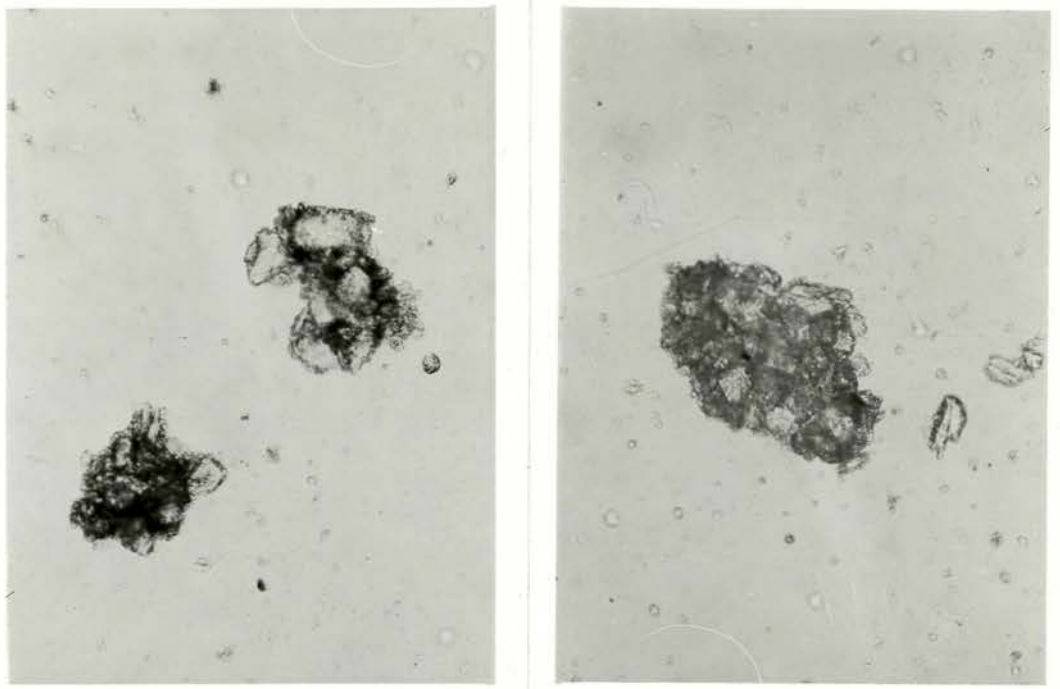
Phosphorus analyses--. Two samples of phosphorus-free seawater and three samples containing 0.24×10^{-6}, 2.96×10^{-6}, and 4.24×10^{-6} moles

Figure 13

Clusters of (a) unstained and (b) stained organic aggregates on the surface of calcite particles. The aggregates formed from filtered seawater upon addition of calcite grains and were stained with Methylene Blue at pH 9. The long dimension of the aggregates is approximately 0.1 millimeter.

Figure 14

Calcite grain coated with organic matter. The accumulation of organic matter is localized on the grain surface. The calcite grain was exposed to filtered seawater for 6 hours. The grain is approximately 0.04 millimeters long.



(a) (b)

Figure 13. Organic aggregates produced by the addition of calcite to filtered seawater.

Figure 14. Calcite grain coated with organic matter.

per liter total phosphorus were obtained by a series of seawater filtrations. The phosphorus was gravimetrically determined as the quinoline complex.

Reagent grade calcite was added in small increments and the pH monitored with time. When the first slight pH change indicated that the critical surface area of calcite (as defined above) was approached, the total amount added was determined. In Figure 15, this amount is plotted against the initial phosphorus concentration; this plot shows a straight line relationship. All samples were phosphorus free after addition of calcite. Surface-active compounds containing phosphorus were presumably removed by the calcite surface. Beyond these immediate conclusions, a more hypothetical interpretation as well as implications of the experimental findings will be discussed in the last section of this chapter.

Implications and Discussion of the Experimental Findings

There are two geochemical consequences of the interpretation of the calcite-seawater equilibration experiments. The saturation state of natural marine waters in contact with skeletal carbonate minerals might not correspond to any equilibrium value determined under certain conditions in the laboratory, calculated from kinetic considerations, or calculated from solution composition. Secondly, the critical calcite surface area indicates concentration of surface-active matter in seawater. Determination of the various critical calcite surface area for different water masses may provide a method for characterizing those waters as specific biological chemical environments.

Carbonate saturation state of natural marine waters

Surface seawater--. The ratio of surface area of suspended carbonate minerals and dissolved surface-active matter rarely reaches such a high value that inorganic chemical interaction between carbonate minerals and seawater is not blocked. Fresh reactive surface area is constantly produced by mechanical breakdown of skeletal carbonates, but the proposed adsorption phenomena rapidly and effectively blocks chemical interaction. Therefore, "apparent" supersaturation of surface seawater can persist for indefinite periods of time (Chave and Suess, 1967). Perhaps most of the sea surface waters are in equilibrium with calcium organic complexes. These complexes are similar in composition and physical properties, regardless of the bulk mineralogy of the carbonate phase. The entire surface of suspended carbonate grains is covered. This explains the "apparent" supersaturation of surface seawater and also accounts for the highly variable distribution of different carbonate mineral phases in surface waters of similar saturation states.

Physico-chemical precipitation--. The inhibition of inorganic chemical interaction between seawater and carbonate minerals also is important to the debate concerning the contribution of physico-chemical carbonate precipitates to the sediment.

Cloud (1962), Broeker and Takahashi (1965), and Milliman (1967), consider physico-chemical aragonite precipitation an important source of sediments in the Bahama Banks.

Stockman, Ginsburg, and Shinn (1967), however, have shown that Penicillus sp. and related species are producing enough aragonite to

account for the carbonate mud deposited in Florida Bay during the past 10,000 years. Neumann and Land (in preparation) make similar estimates for the Little Bahama Bank. Lowenstam and Epstein (1957) emphasized earlier that the bulk of aragonite needles is biochemically produced.

The effect of organo-carbonate associations on the calcium carbonate equilibration indicates that physico-chemical precipitation of aragonite or any other calcium carbonate phase may be insignificant compared to biochemical production by organisms.

Interstitial waters--. Berner (1966a) analysed more than 100 interstitial water samples from Bermuda and Florida Bay sediments. Saturometry measurements showed equilibrium with respect to calcite and undersaturation with respect to aragonite and Mg-calcite. The latter minerals are the dominant phases of the sediments. Berner attributes the lack of equilibrium to interaction of dissolved Mg^{++} ions with the surfaces of the minerals. Organic coatings, such as form on artificially introduced carbonate surfaces from interstitial waters, may also cause the apparent disequilibrium between a variety of carbonate phases and the adjacent water. Direct evidence of organic coatings on carbonate sediments will be presented in the next chapter.

Adsorption of organic matter from seawater by calcite as an analytical method

Characterization of chemical-biological environments--. Different marine environments can be described by the concentration of surface-active compounds for which the only source is marine organisms. The concentration of these compounds may be measured by the adsorption method as described above. Therefore, a relationship can be established between

biological activity and calcium carbonate reactivity. Regional distribution of organic-rich waters could be mapped by this adsorption method, as shown for Bermuda and Long Island surface waters, and extremely organic-poor waters could be identified.

Composition of particulate and dissolved organic matter--. Existing methods of concentrating dissolved organic matter from seawater by adsorption are supplemented by the use of solid calcium carbonate. Bader, Hood, and Smith (1960) suggested adsorption on clay minerals for recovering dissolved organic compounds from seawater. Davenport (personal communication) used clay-size bentonite to concentrate RNA from seawater. Coprecipitation of dissolved organic matter with ferric hydroxide is based on surface phenomena.

Calcium carbonate as an adsorbent might be more specific for fatty acids, alcohols, and esters, and would therefore be useful in determining the concentration of these compounds. Adsorption onto calcium carbonate should not affect other compounds such as soluble carbohydrates or free amino acids.

Elemental analyses may be further developed for adsorption phenomena in seawater. An example is presented below using the relationship of total phosphorus and critical surface area of calcite as shown in Figure 15.

Assuming that surface-active compounds, both containing phosphorus and phosphorus-free, adsorbed at the carbonate seawater interface, the straight line relationship may be extrapolated and its intercept with the phosphorus concentration axis is taken as a measure of the total concentration of surface-active compounds.

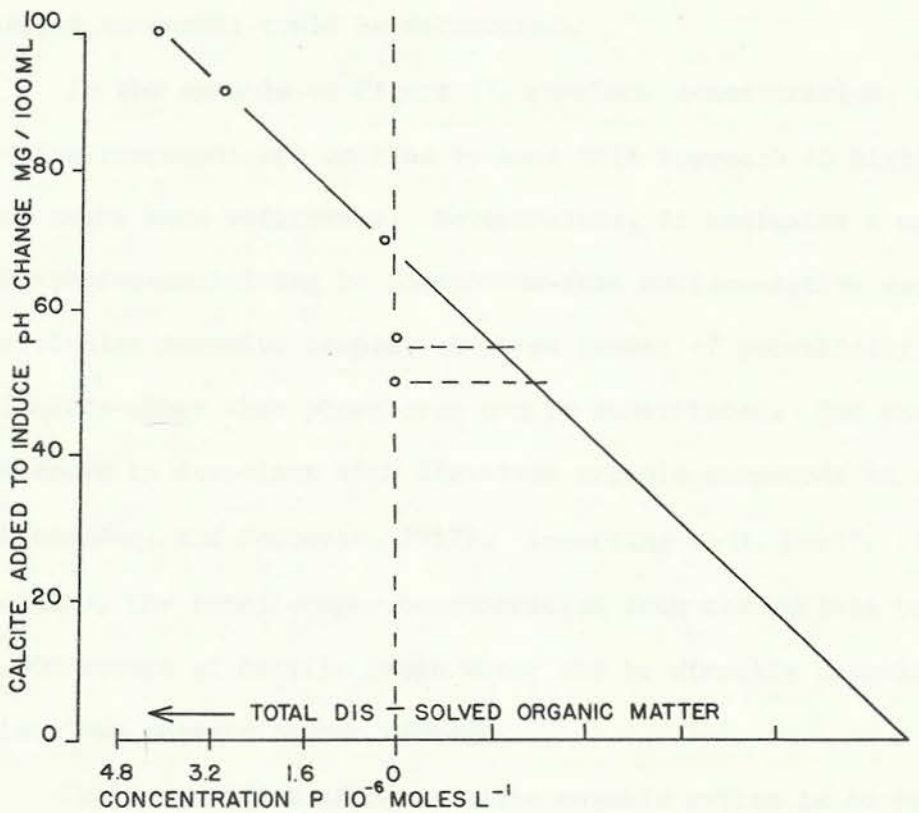


Figure 15. Adsorption of phosphorus-containing organic matter by calcite.

The two samples which initially were phsophorus-free, but still required 50 mg calcite to induce inorganic reaction, could thus be placed on the extension and their respective total concentrations of surface-active compounds could be determined.

In the example of Figure 15, absolute concentrations of total surface-active compounds are omitted because this approach is highly speculative and needs more refinement. Nevertheless, it indicates a ratio of 1:2 for phosphorus-containing to phosphorus-free surface-active compounds in this particular seawater sample. A large number of potentially indicative elements other than phosphorus can be substituted. For example, copper is known to associate with dissolved organic compounds in seawater (Alexander, and Corcoran, 1967). According to D. Hurd's (1968) preliminary results, the total copper concentration from the surface to a depth of 3,000 meters of Pacific Ocean water can be directly correlated with the dissolved organic carbon content.

The composition of particulate organic matter is as yet not clear. Gordon (1967, personal communication) demonstrated proteinateous and carbohydrate compounds by use of Bromophenyl Blue stain. Carboxyl-groups of proteins, polyphosphates, phospholipids or other complex lipids, and sulphate-groups of mucopolysaccharides are perhaps constituents of organic aggregates as indicated by the Methylene Blue stain of this study. This information may be supplemented by the use of elemental analyses for phosphorus, and of sorption analyses for surface-active compounds.

Cycle of surface-active compounds

The scientific implications of sorption, elemental analyses, and staining techniques, may best be demonstrated by discussing a natural cycle of surface-active compounds. This idea was first suggested by Chave (1967, personal communication), and some of his observations are included here. As many steps as possible are documented in this cycle. (See Figure 16.) Some, however, are purely hypothetical, some may never be documented, and a few might just be wrong.

The cycle consists of a central part which is the oceanic environment. The ultimate source of all organic matter is organisms. The organic matter exists in the dissolved and particulate states which form a steady state system (Riley, 1963). The two major pathways from the dissolved to the particulate state involve the air-water and solid-water interface. These pathways are perhaps irreversible or, at least, they dominantly transform dissolved matter into particulate matter. Adsorption at the air-sea interface is experimentally demonstrated by Baylor, Sutcliffe, and Hirschfeld (1962); Sutcliffe, Baylor, and Menzel (1963); and MacIntyre (1965).

Association of organic matter at the solid-seawater interface was first observed by Chave (1965); Wangersky and Gordon (1965). Adsorption of organic matter on calcite surfaces was experimentally shown by Chave and Suess (1967) and is applied in this study. Particles formed on bubbles and on mineral surfaces are utilized as food by zooplankton. Subsequent metabolic products replenish the reservoir of dissolved surface-compounds. The organisms also transform a significant amount of surface-active matter into CO_2 and H_2O.

At the sea-air interface, there is a high concentration of surface-active compounds as described by Garrett, Jarvis and associates. This interface is also the site at which surface-active compounds leave the oceanic part of the cycle in the form of aerosols (Blanchard, 1964). Most of the aerosols eventually reach the air-water interface again and form part of a smaller atmospheric cycle; some reach the land as condensation nucleii in rain. From land, the pathway is completely hypothetical. It is assumed that surface-active matter is carried back into the oceanic system partly by runoff. Whether this material is in dissolved or particulate state, or whether any important intermediate processes remove material through oxidation, is unknown. The latter possibility is indicated on the graphic representation of the cycle as $CO_2 + H_2O$.

The solid-water interface also represents a site at which the surface-active compounds leave the oceanic cycle. They accumulate as part of the sediment. There is, perhaps, an undetected exchange of surface-active compounds with the overlaying seawater via intersitital water. Another irreversible loss from the cycle is caused during fresh water diagenesis with subsequent uplift of the sedimentary rock. Beach rock formation, and other free chemical interaction occurring in carbonate sediments exposed to fresh water, may be interpreted as indirect evidence for removal of protective coatings. Initial grain coatings may be preserved in rocks or concentrated through interstitial water transport to become petroleum. The pathways during weathering are again unknown, but they likely are oxidation and transportation to the ocean in the form of particulate and dissolved matter.

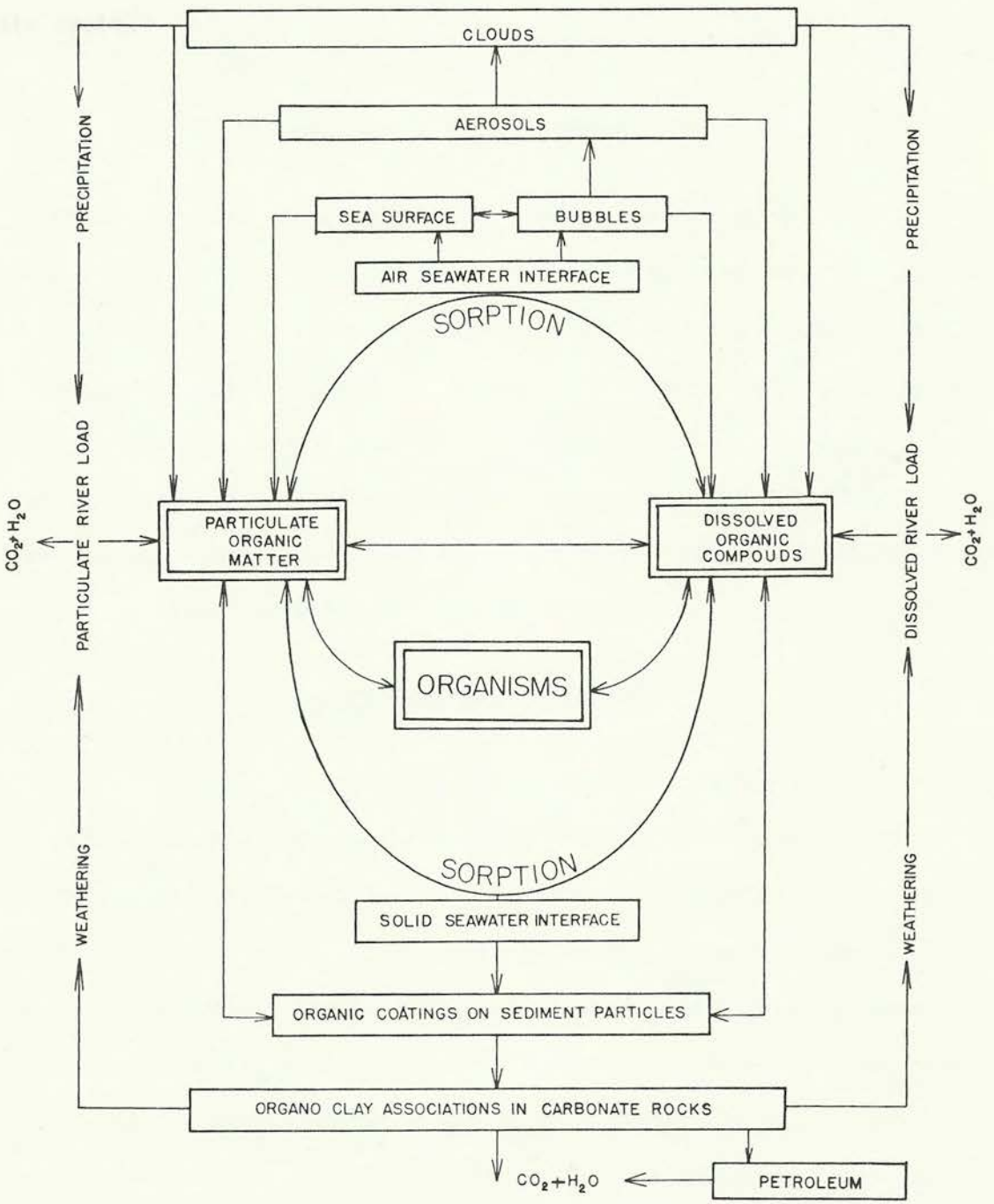


Figure 16. Cycle of surface-active compounds in nature.

Along the different pathways, loss of surface-active compounds occurs through chemical or bacterial oxidation. Hopefully, some of the analytical methods suggested will help clarify the unknown pathways of this cycle.

IV. ORGANO-CARBONATE ASSOCIATIONS IN SEDIMENTS AND ROCKS

Natural organo-carbonate associations occur on suspended carbonate material, on Recent carbonate sediments, and on diagenetically altered Pleistocene, Jurassic, and Mississippian carbonate rocks.

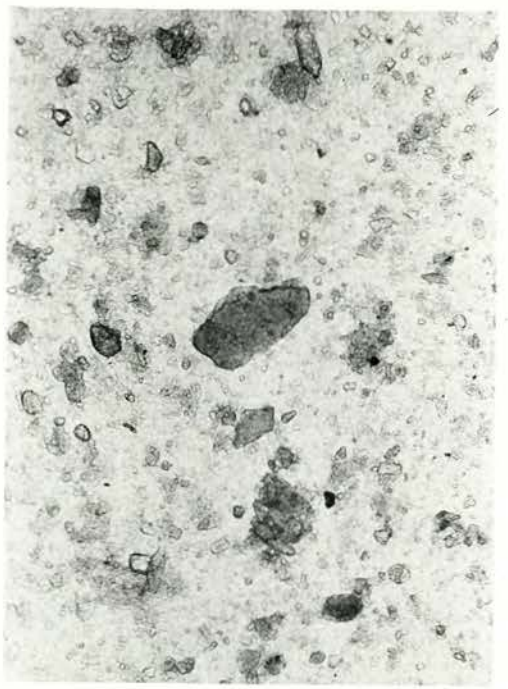
Suspended Carbonate Minerals

Mineralogy and distribution of suspended carbonate minerals in surface waters from four parts of the Atlantic ocean are summarized by Chave and Suess (1967). In all cases, the carbonate sources can be identified as planktonic organisms, reef organisms, and resuspended bottom sediments. Figure 17 shows suspended carbonate minerals enclosed in organic aggregates which were filtered from Bermuda surface waters. They may have developed as a monomolecular surface film or complex, followed by aggregation of smaller particles and populated by bacteria.

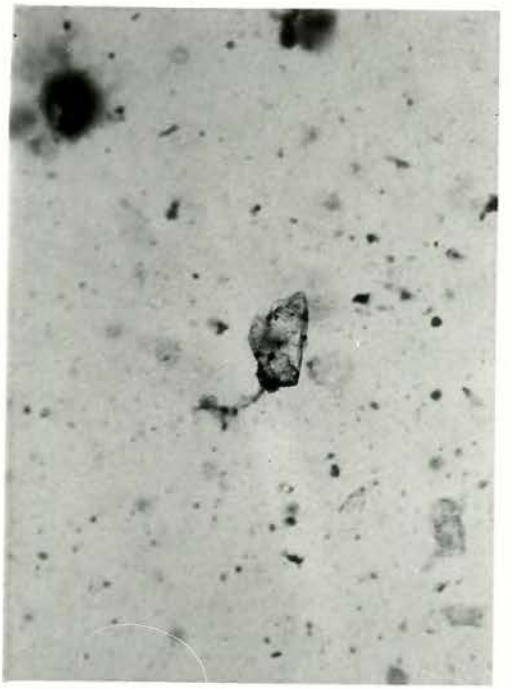
Recent Carbonate Sediments

Lack of transformation of unstable minerals

All Recent shallow-water carbonate sediments are mixtures of different mineral phases. They contain 50-90% metastable aragonite and/or Mg-calcite. The undersaturated state of interstitial waters shows no reaction of metastable minerals. Chave (1962) and Neumann (1965) propose inorganic chemical interaction of sediments and interstitial water because of a decrease of chemically unstable phases with decreasing grain size. Berner (1967), however, found in Florida Bay sediments that $Mg\text{-}calcite_{(0.14)}$ and aragonite constituted the finest fraction of less than 0.4 microns, and $Mg\text{-}calcite_{(0.06)}$ and aragonite were found in coarser fractions



(a)



(b)

Figure 17. Suspended carbonate minerals from Bermuda surface seawater, associated with organic matter.

(a) The dark areas indicate organic matter on the carbonate mineral surface. The large grain is approximately 0.1 mm long.

(b) Suspended carbonate mineral grain with stained organic matter. A 0.1% Methylene Blue solution was used for staining and the pH was adjusted to 9 with NaOH in order to prevent dissolution.

(0.4-2.0 microns and 2-5.0 microns). Whichever distribution exists, it does not seem to be related to simple physico-chemical dissolution. Ginsburg et al. (1967) found cemented reef detritus and "inorganically precipitated" vug fillings of Mg-calcite$_{(0.18)}$ in living Bermuda reef structures. Friedman (1966) reported Mg-calcite from deep-sea sediments. Fischer and Garrison (1967) described globigerina ooze, from the eastern Mediterranean Sea and off Barbados, cemented by Mg-calcite$_{(0.13)}$.

Berner (1966a, 1966b, 1967) and Weyl (1967) have advanced an explanation for the existence of metastable carbonate mineral assemblages by hypothesizing that aqueous Mg^{++} ions interact with the mineral surfaces. This viewpoint is **discussed** and compared to the organic coating theory.

Organic coatings on Recent carbonate sediments

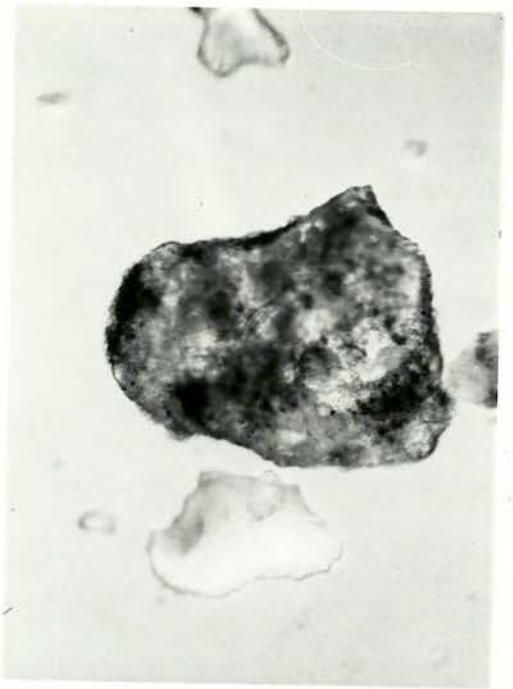
Microscopic examination of carbonate sediment shows that a significant portion consists of brownish organic aggregates which enclose many clay-size carbonate grains and are dispersed throughout the sediment. They are probably the slowly settling organic aggregates of the oceanic suspended load. Staining with 0.1% Methylene Blue at pH 10 revealed that more than 90% of the total grain surface of all grain sizes is covered with a visible organic coating. Variation in color intensity suggests either different compounds in the organic layer or variable thickness. Edges and corners usually are not as well stained--perhaps a result of handling of the samples. In Figure 18, a + b silt-sized skeletal carbonate particles are shown with Methylene Blue stained organic coatings. These coatings were oxidized by heating for five to six hours in 30% H_2O_2 at pH 9 adjusted with NaOH. Staining after this treatment showed markedly reduced results as indicated in

Figure 18

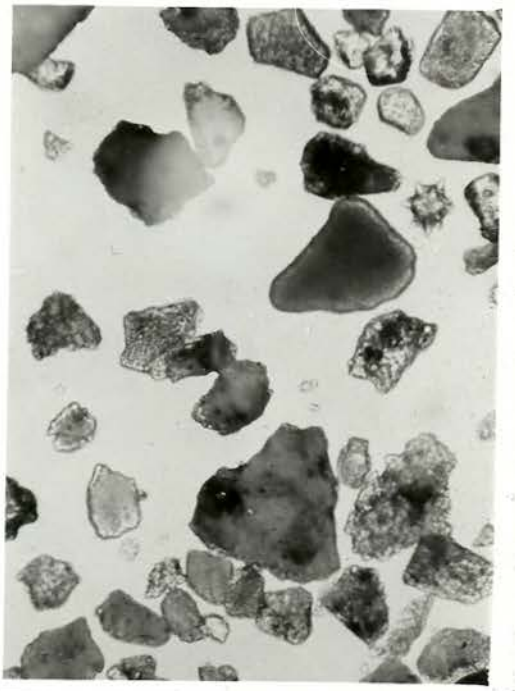
(a) Silt-size skeletal carbonate grain with organic matter. The organic coating is stained with Methylene Blue at pH 10. The grain is 0.1 mm long.

(b) Sediment particles enclosed in organic matter. More than 90% of the carbonate mineral surface of all sediment particles is coated by organic matter.

(c) These sediment constituents have been treated with hydrogen peroxide to remove organic matter before staining with Methylene Blue. The large grains are 0.1 mm long. The photomicrographs were taken in a combination of transmitted and reflected light.



(a)



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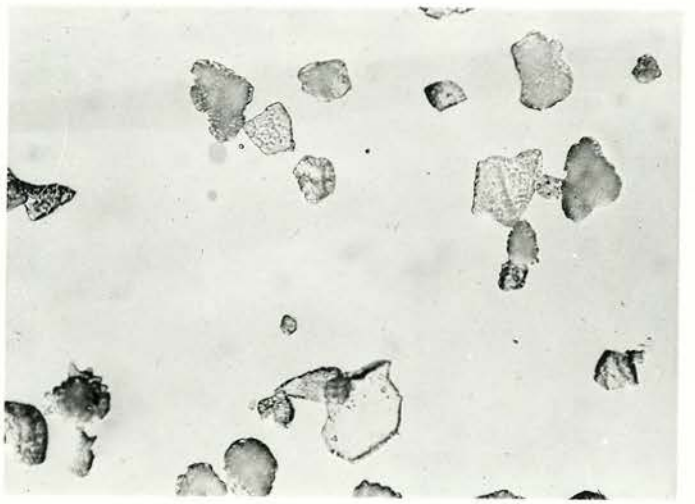


(c)

Figure 18. Carbonate sediments stained for organic matter by Methylene Blue.

Figure 18 (c). Most of the grains were clean and unstained; however, quite a few coatings withstood oxidation, at least locally. Some coatings were reduced to patches and spots, especially in corners or on particularly rough surfaces. Another example of organic coatings on Recent carbonate sediments is described and illustrated below. Methylene Blue was again used for staining the organic portions.

An "algal biscuit" was collected from Kailua Bay, Oahu, Hawaii, and kept alive for three weeks in a small seawater tank. Every two to three days, it was sprinkled with calcite, aragonite, and mixed carbonate sediments of various grain sizes. The algal filaments which form a continuous film between sediment layers and penetrate as single fibers through the layers were stained dark blue. As shown in Figure 19, proteinaceous and phosphate-containing material surrounds the mineral particles. Most grains were enclosed in a pink-blue coating. According to this color, the coating is characterized by reactive SO_4^{2-} groups. Mucopolysaccharides, $SO_4^{=}$-containing polysugars, are secreted by algae as a sheath of mucus. This mucus seems to trap sediment particles which form the inorganic portion of the layered structure of modern algal biscuits and fossil stromatolites. Corals are known to secrete the same kind of mucus, and Johannes (1967) estimated a production of 20 milligrams per m^2 per hour. It is therefore possible, by differential staining technique, to characterize sediment particles by the environment in which they have been coated.

Carbonate sediment seawater interaction

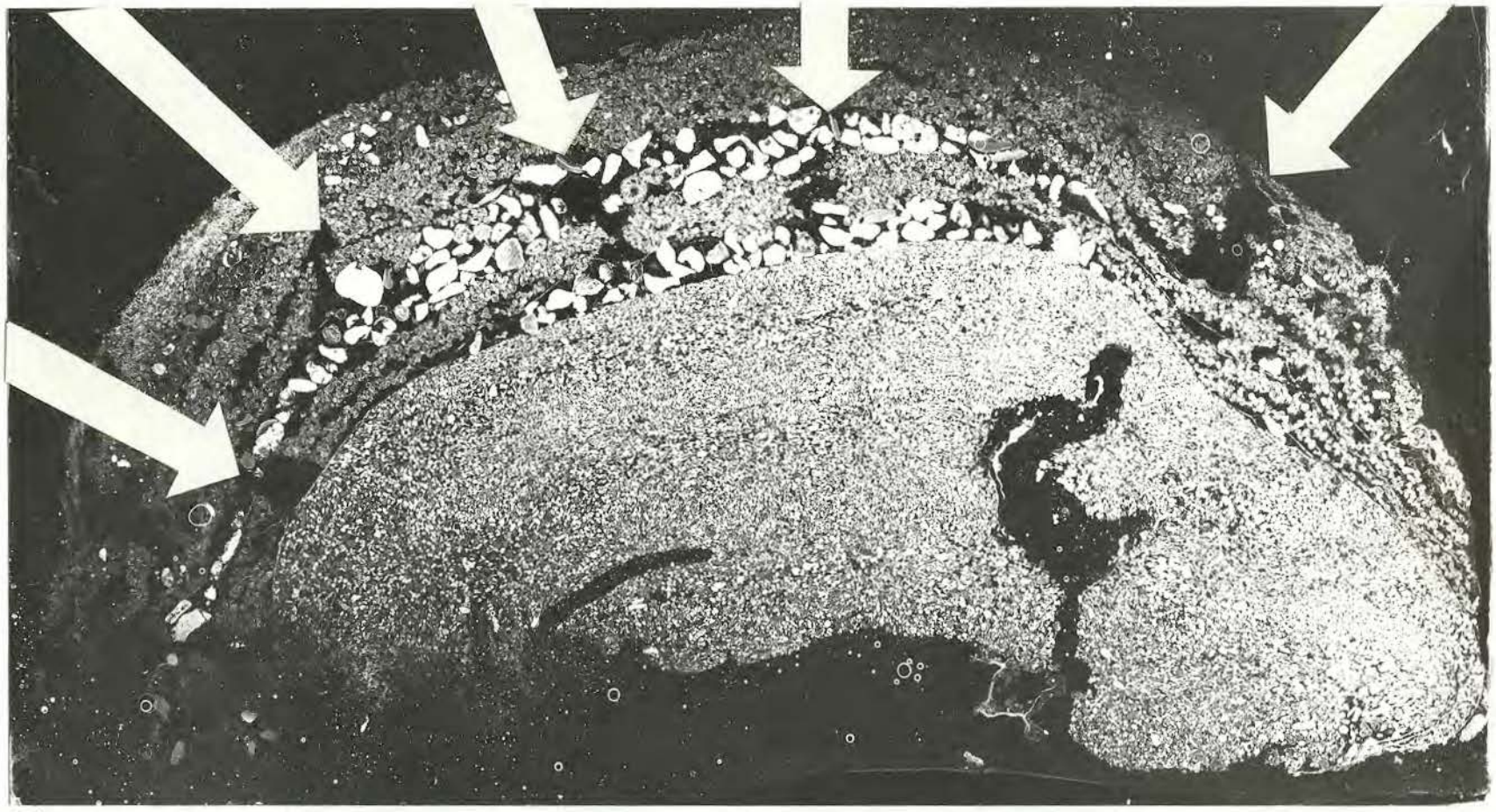
In order to test the "reactivity" of sediments, coated and uncoated carbonate grains were brought into contact with CO_2-enriched seawater of

Figure 19

(a) The lower dense portion of the algal biscuit grew in nature; the upper portion was developed in a seawater tank over a period of three weeks by adding mixed carbonate sediments to the growing biscuit. The radial irregular channels marked by arrows indicate bubble trains through which photosynthetic oxygen escaped during the day. These escape channels remained in place and open while the biscuit grew in undisturbed water.

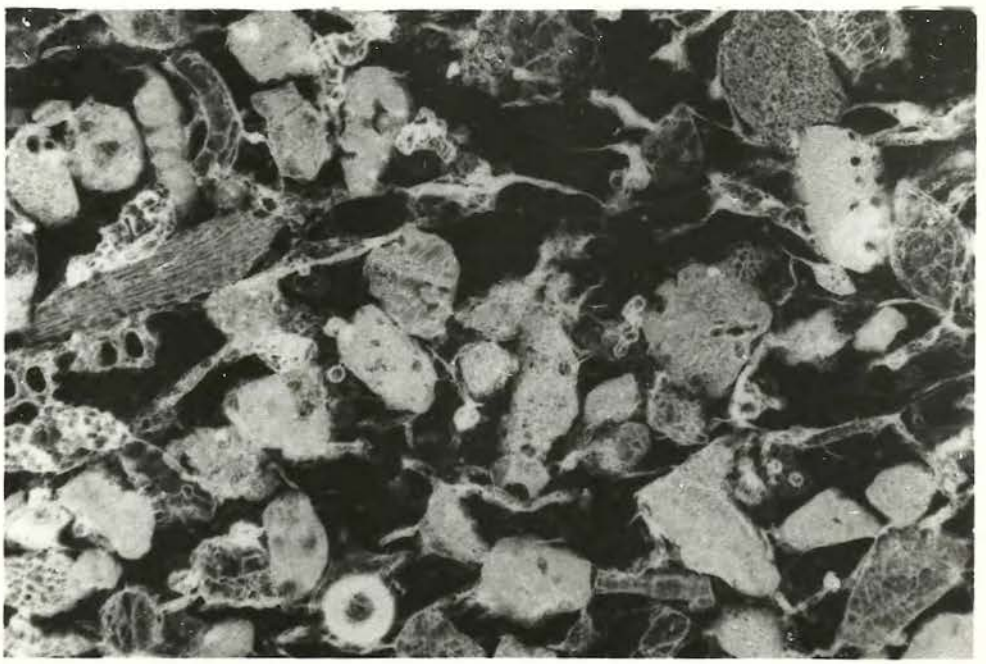
(b) Enlargement from the dense portion. The organic matter of the algal filaments is stained by Methylene Blue. These filaments enclose individual grains and form horizontal organic layers.

(c) Enlargement from the portion grown in the seawater tank. Note the horizontal lining and vertical penetration of algal filaments. Some of the carbonate grains are enclosed in coatings of mucopolysaccharides (?) as suggested by the characteristic pink color of the Methylene Blue reaction with $SO_4^{=}$ -containing organic compounds.



(a)

Figure 19. Cross-section through an "algal biscuit".



(b)

(c)

Figure 19 continued.

pH 7.5 to 7.7 at a large solid-to-water ratio. This water was undersaturated with respect to calcite. It was possible to maintain undersaturation at atmospheric P_{CO_2} over a long enough period to perform the equilibration experiments (20-30 minutes) because of slow kinetic CO_2 evolution.

The large solid-to-water ratio prevented recoating through adsorption. The pH-electrode was immersed into the sediment and the change of H^+ ion concentration monitored. Eighteen samples from the Bermuda platform were equilibrated by the saturometry technique described above. Series A of the 18 samples consisted of fresh sediments; whereas, the samples in Series B were boiled in 30% H_2O_2 for 2-3 hours. (Detailed experimental procedure is in Appendix IV.) Figure 20 shows the sample locations and Table XIII, the results.

The untreated natural samples showed negligible reaction with the undersaturated water within 30 minutes. The H_2O_2-treated portions of each sample dissolved as was indicated by a pH increase. The increase of pH over a constant period of time is an effect of grain size and mineralogy, rather than an indication of equilibrium. The average Mg content of the calcite was determined by x-ray diffraction using fluorite as an internal standard. The ratio of aragonite to calcite was estimated from integrated peak areas, as described by Chave (1962).

Figure 21 quantifies the observed "reactivity" of the uncoated samples as related to the average magnesium content and to the percentage of Mg-calcite. It appears that a constant ratio of calcite to aragonite and an increase of magnesium in the calcite portion causes increased pH change. The same is true for constant magnesium content with an

Figure 20

The samples represent three main environments of carbonate deposition. Samples marked SR and NR are from the South and North Reefs of the Bermuda platform. Samples marked CH and HS represent the deposits of an enclosed lagoon.

There are all gradations between the main environments. For example CH1, CH2, and NL1 show strong mineralogical influence from the nearby reef areas. HS1 and NL5 are from small environments of local characteristics. For mineralogy of the sediments, see Table XIV.

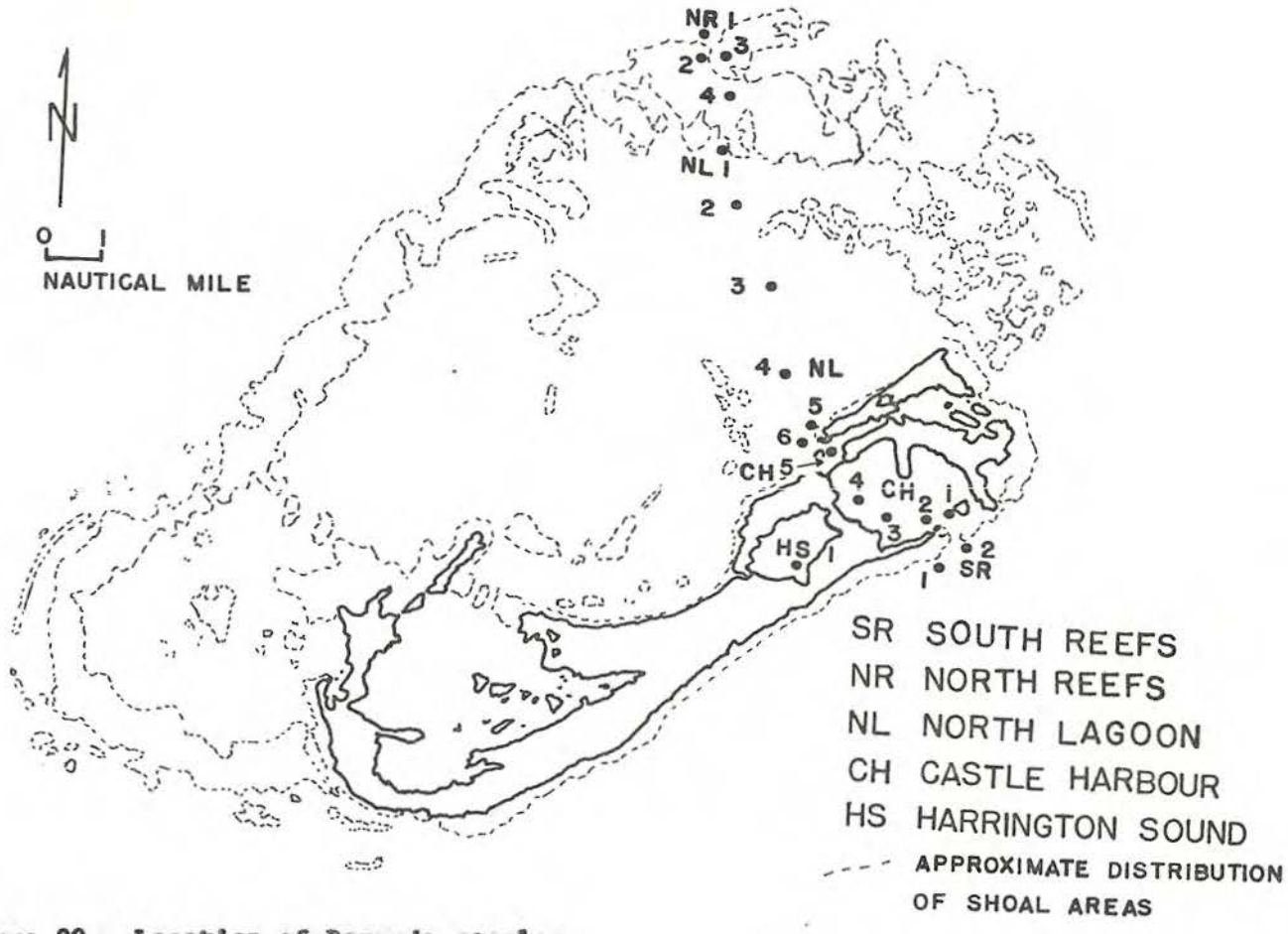


Figure 20. Location of Bermuda samples

Table XIII. Carbonate sediment-seawater reactions.

Sample #	Interstitial pH	Calcite %	Aragonite %	Magnesium mole%	Fresh sediment pH	H_2O_2-treated pH
SR1	8.14	89	11	15	7.90 - 7.92	7.73 - 8.45
SR2	7.80	49	51	13	7.79 - 7.90	7.74 - 8.26
CH1	7.92	61	39	13	7.83 - 7.85	7.82 - 8.45
CH2	7.90	62	38	13	7.76 - 7.83	7.80 - 8.40
CH3	7.60	31	69	13	7.66 - 7.63	7.65 - 8.03
CH4	7.65	44	56	12	7.70 - 7.74	7.70 - 8.08
CH5	7.80	42	58	16	7.80 - 7.81	7.80 - 8.32
NL6	7.75	45	55	16	7.81 - 7.83	7.80 - 8.27
NL5	7.78	45	55	14	7.77 - 7.78	7.78 - 8.14
NL4	7.50	25	75	13	7.65 - 7.55	7.66 - 8.02
NL3	7.74	33	67	16	7.73 - 7.74	7.74 - 8.06
NL2	7.71	14	86	17	7.74 - 7.71	7.72 - 8.02
NL1	7.70	42	58	14	7.70 - 7.70	7.71 - 8.09
NR4	7.74	48	52	14	7.74 - 7.76	7.76 - 8.22
NR3	7.94	28	72	13	7.93 - 7.94	7.95 - 8.29
NR2	7.79	47	53	13	7.78 - 7.80	7.79 - 8.55
NR1	7.90	56	44	14	7.94 - 7.94	7.95 - 8.45
HS1	7.73	70	30	5	7.73 - 7.76	7.72 - 7.90

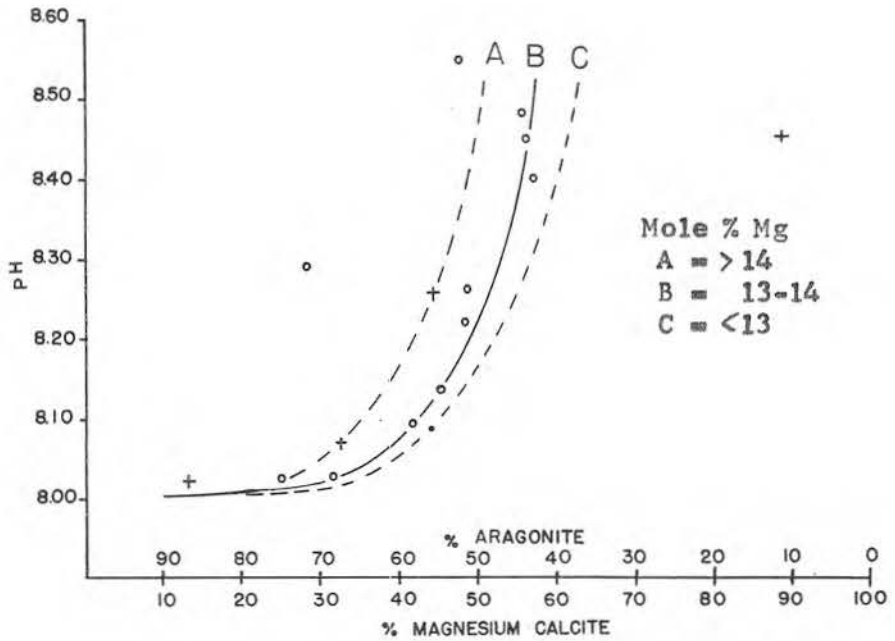


Figure 21. Reaction of carbonate sediments with undersaturated seawater.

increase in Mg-calcite percentage. This relationship indicates that simple dissolution reaction between the undersaturated seawater and the carbonate sediments takes place as predicated from the mineralogy.

According to Schmalz (1967), the most soluble phase of a carbonate mixture determines the equilibrium pH of seawater over a long period of time. This was not apparent in the above experiments; but given enough time, the sediments would perhaps have equilibrated with the undersaturated seawater--each to a pH corresponding to its most soluble phase. These values are clearly different from the pH of interstitial waters in the natural environment of sedimentation.

It can be concluded that shallow-water carbonate sediments are

coated with an organic layer and, therefore, do not interact freely with the interstitial water. The organic layer can be stained with Methylene Blue and can be removed by H_2O_2 treatment. Free dissolution reactions with undersaturated water take place as would be expected from the mineralogy and grain size of the sediment after removal of the organic matter.

Distribution and resistance of natural organic coatings

H_2O_2 treatment destroys the coatings to such an extent that inorganic chemical interaction is no longer blocked. But this procedure does not entirely remove the coating, as indicated by the Methylene Blue stain.

Sediments exposed to interstitial water of pH 6.3 and lower will probably interact chemically. This has been shown for sediments which were excessively washed in distilled water, wet-sieved, or mechanically treated in any other way. It is not surprising that the importance of organic matter in carbonate sediments, as coatings or as aggregates, has not received more attention since most of the post-sampling treatments involve extensive washing, cloroxing, H_2O_2 treatment, and ultrasoneration. Under these conditions the chemical inhibition is destroyed and substantial parts of the coatings are removed.

The actual processes which affect the stability of coatings can only be assumed and need further investigation. As a first approximation, they appear to be:

1. Dissolution of the protective coating as a result of increased hydrogen ion concentration,
2. Oxidation of organic material into $CO_2 + H_2O$,

3. Mechanical abrasion caused by extensive handling,

4. Dilution due to desorption.

The regional and vertical distribution of coated carbonate particles in sediments has been demonstrated by the eighteen samples from various environments, described above, and by staining techniques on samples of a 130 cm core from an enclosed lagoon, Castle Harbour, Bermuda. All samples show complete coating and no significant variation between environments can be detected as yet.

Alternate hypothesis

A model accounting for disequilibrium between carbonate particles and seawater is discussed here.

Weyl (1967) and Berner (1966a, 1966b, 1967) advanced a model based on interaction of aqueous Mg^{++} ions with the carbonate surface. Weyl reasoned from a great many equilibration experiments between carbonate minerals and seawater that the mineral surface adjusts itself gradually in supersaturated seawater by depositing Mg-rich overgrowth. He considered that over prolonged periods of time, recrystallization is responsible for elimination of the chemical difference between the overgrowth and the bulk mineral. In undersaturated waters, the supersoluble overgrowth redissolves layer by layer until that particular layer is reached which has a composition in equilibrium with the seawater of the new environment. The thickness of the overgrowth varies with the degree of supersaturation of the surrounding waters; but it is never much more than 100 Å thick, so it can not be directly observed under the optical microscope.

The model is based partly on observed differences of reaction on rates of carbonate minerals in Mg^{++}-containing solutions. But there is no indication that these minerals reach a different final equilibrium (Weyl, 1967, Figure 2). This has also been confirmed by Berner (1967), who showed that calcite and dolomite each have a common ion-activity product ($10^{-8.37}$ and $10^{-17.0}$, respectively) in the presence and absence of high Mg^{++} concentrations in distilled water. Therefore, the "model experiments" in controlled systems do not produce supersaturation of the solution with respect to calcite in the presence of magnesium.

Berner (1966b) has further shown that Mg^{++} is held with different degrees of bonding by the surface of natural, clay-size carbonate sediments in exchangable positions with Ca^{++}. He argues that part of the Mg^{++} constitutes a more soluble surface layer and is directly responsible for the anomalous solution behavior of carbonates in seawater. However, Berner observed ion exchange capacity of carbonates, with respect to aqueous Mg^{++}, only on <u>natural</u> sediments which did not undergo grinding or any other serious surface damage. He considers exchange capacity of organic matter and has determined it to be 10% of the total capacity, but it is here suggested that the contribution of the organic coatings is largely responsible for the ion exchange capacity. Between 86% and 97% of the sites of the total cation exchange capacity of silt-size and clay-size estuarine deposits are located on the oxidizable organic fraction of Hudson River sediments (McCrone, 1967).

Berner (1967) also considers two models for surface interaction of Mg^{++} and carbonate minerals. One is based on an ideal dolomite-like ($Mg\text{-carbonate}_{0.05}$) nonexchangeble surface layer, and the second model

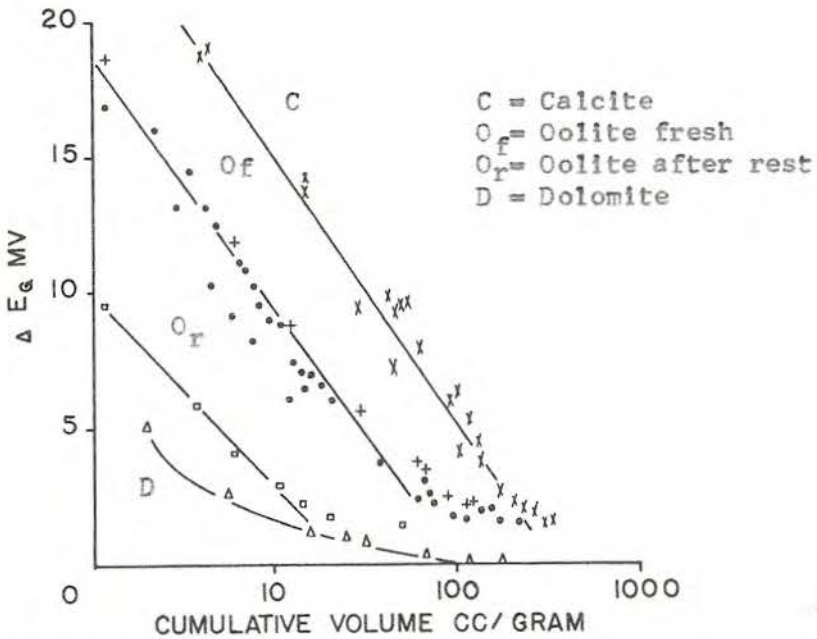


Figure 22. Reaction of carbonate minerals with seawater. Weyl, 1967, The solution behavior of carbonate materials in seawater. Stud. Trop. Oceanogr. Miami 5, pp.791-800.

assumes an ideal exchangeable surface layer, rich in magnesium, in contact with 0.1 molar $MgCl_2$ solution (seawater = 0.05 molar). The two models do not predict the equilibrium conditions of natural carbonate sediments in $MgCl_2/CaCl_2$ solution.

Figure 22 contains some of the results of Weyl's (1967) initial experiments on solution behavior of carbonates in seawater. Weyl (1967) precipitated calcite by flowing seawater at a given rate through a column packed with carbonate minerals. He monitored the reaction in terms of potential change.

This potential change is plotted in Figure 22 against the cumulative volume of seawater per gram pumped through the column filled with solid

carbonate. The potential difference is positive; therefore, there is precipitation on the carbonate minerals due to the continuous flow of seawater.

At high solid to water ratios (1 gram of solid per 2-10 ml of seawater), very fast precipitation takes place. With increasing volume of water, this rate slows down and eventually ceases. It does not remain constant as Weyl infers. It is not of primary interest whether a linear decrease of reaction rate or a marked rate change occurs, as most of the low solid to water ratios indicate. It is more important that the reaction rate approaches zero. The decreasing reaction rate intersects the ordinate at different volumes of seawater per gram of solid.

The dolomite seawater reaction ceases after 100 ml of water has been in contact with the surface of 1 gram of solid. Extrapolation of the oolite samples indicates termination of the precipitation reaction between 400 and 1000 ml per 1000 mg of solid. The surface area of the carbonate minerals used in these experiments is approximately 100-200 cm^2 per gram. This value was calculated from the average grain size of these carbonate minerals which was given in Weyl's publication. A ratio of 0.02 - 0.04 m^2 of calcite surface to one liter of seawater can be calculated at the termination of the inorganic reaction.

The specific surface area for powdered calcite, used in the experiments described in Chapter III, is 0.8 - 0.7 m^2 per gram. At the beginning of the inorganic reaction a ratio of 40 milligrams per 200 millliliters was recorded. This ratio represents 0.14 m^2 of calcite surface per liter of seawater and is within one order of magnitude of

the value obtained from Weyl's flow experiments. The specific surface area for calcite estimated in Weyl's study is a minimum value; whereas, the 0.7 m^2 per gram used in this study was determined by argon adsorption and represents a maximum value.

Accordingly, Weyl's results may be interpreted with the organic coating hypothesis. Figure 22 indicates that inorganic precipitation from seawater ceases after the dissolved surface-active content of a particular volume of seawater is used up on formation of organic coatings. This particular volume of seawater is characteristic for the condition of the carbonate mineral surface. Apparently, in the case of dolomite only the calcium sites are affected because the particular volume necessary to inhibit inorganic reaction is very small. Fresh oolite surfaces and those previously soaked in seawater differ markedly with respect to the precipitation reaction. The surfaces of the latter were coated to a larger extent prior to measured precipitation reaction. The decrease in rate of reaction observed by Weyl is, presumably, a function of the decrease in free surface area due to formation of organic coatings.

The model of organic interaction of aqueous Mg^{++} ions takes into account only situations in which precipitation occurs immediately upon contact of carbonate surface and solution. In cases where the seawater is undersaturated with respect to carbonate phase, no precipitation of Mg-rich overgrowth can take place. Therefore, those phases should dissolve completely. The persistence of Mg-calcite$_{(>0.10)}$ as suspended minerals, aragonite, and Mg-calcite$_{(>0.06)}$ in undersaturated interstitial waters cannot be explained by this theory.

Recent carbonate deposition

In a review of Recent carbonate sediments, Chave (1967) characterized the conventional geological concept of carbonate sedimentation as implying that carbonate sediments are rare or absent at latitudes of greater than 30 degrees. Other inferences are that beyond the "compensation depth" of about 4,000 meters no carbonates are found in pelagic sediments, that carbonates are deposited in "a warm shallow sea", and that formation, deposition, and distribution of carbonate sediments are controlled by inorganic chemical processes. Obvious reef deposits are the exceptions to this general inorganic theory.

One of the major conclusions of studies concerning marine carbonate sedimentation was that the majority of sediments are biogenic in origin (Illing, 1954; Ginsburg, 1956; Lowenstam and Epstein, 1957; Stehli and Hower, 1961; Chave, 1954a, 1954b; Imbrie and Purdy, 1962; Korniker and Boyd; Hoskin, 1963; Taft and Harbaugh, 1964. Apparently such important work as that of Vaughan (1918), Goldmann (1926), and Thorp (1935) did not impress most of the geologists of that time.

Secondly, important geochemical studies of carbonate behavior in seawater contributed information to a new concept of carbonate deposition (Garrels and Thompson, 1962; Chave et al., 1962; Chave and Schmalz, 1966; Berner, 1966a, 1966b, 1967). Fischer and Garrison (1967) indicate in an introductory remark that the "new concept" implies that:

(1) calcite is not precipitated from seawater by inorganic means;

(2) induration and lithification of carbonate sediments cannot occur on the seafloor, but require either diagenesis in fresh water or burial to great depth.

Before the "new concept" could finally be formulated or even agreed upon, numerous observations were reported which were extremely difficult to incorporate. For example, inorganic formation of aragonite, calcite, dolomite, and Mg-calcite$_{(>0.10)}$ in modern reef structure, deep sea sediments, and other seawater-covered carbonate sediments indicate uninhibited inorganic reactions between seawater and carbonate mineral phases (Illing, Wells, and Taylor, 1965; Shinn, Ginsburg, and Lloyd, 1965; van der Borch, 1965; Friedman, 1965; Ginsburg, Shinn, and Schroeder, 1967; and Fischer and Garrison, 1967).

Some of the workers on Recent carbonate sedimentation will perhaps interpret these "newest" observations to indicate that the "conventional view" of inorganic carbonate precipitation and dissolution was not so bad after all. It must be pointed out, however, that although calcite and dolomite form as stable phases, aragonite and Mg-calcite$_{(0.05-0.18)}$ precipitate as metastable phases. This complicates the situation even further. Instead of supporting the inorganic theory, it gives evidence for incompatible processes which cannot be described by one general theory.

Penecontemporaneous formation of dolomite and calcite as well as solubility determinations of carbonate minerals in seawater indicate true equilibrium conditions. Disequilibrium conditions are indicated by lack of diagenetic transformation of aragonite and Mg-calcite$_{(>0.05)}$, penecontemporaneous formation of these phases, and the presence of metastable suspended minerals in seawater. This study attempts to show that at least some of these processes may be explained by interaction of the carbonate surface with dissolved organic matter.

It may be assumed that simple inorganic processes of dissolution and precipitation take place under conditions at which organo-carbonate associations are unstable. Simple inorganic processes are inhibited in the presence of organo-carbonate associations. The applications of this theory cannot easily be tested because a complete new kind of data are needed. This data should contain information describing biological activity, abundance of marine life, concentration of surface-active compounds, and chemical and mineralogical information.

Limestone diagenesis

The ubiquitous organic coatings on carbonate particles of Recent sediments assert a strong influence upon post-depositional processes, some of which have been discussed in the first section of this chapter. Limestones with textural characteristics resulting from originally coated sediment particles are of interest to geologists. Incomplete, inhibited, differential, and selective recrystallization or replacement may be attributed to effects of organic coatings. Such textures are investigated petrographically and with microchemical staining techniques in order to give some examples of how organic coatings may be detected.

Adsorption of Methylene Blue by clays (Plesch and Robertson, 1948; Taylor, 1967) strongly interferes with the direct application of the organic staining techniques. It can, therefore, be used only with H_2O_2 treatment of the samples to evaluate the uptake of Methylene Blue by the clay fraction in the presence and absence of organic matter.

Terminology

Organic coatings affect only those diagenetic processes in which the solution and the mineral surface react together.

Precipitation of calcite cement, as described by Land (1967), and micro-processes of aragonite-calcite transformation, as well as macro-dissolution of aragonite and Mg-calcite are affected by the presence of organic coatings. The latter diagenetic process is identical to Bathurst's (1964) replacement or micro-dissolution precipitation. Recrystallization (census strictu), which implies grain enlargement due to the small particle solubility effect, may be inhibited by organo-carbonate associations (Pantin, 1965). Precipitation of and cementation by calcite in primary and secondary pore space is another diagenetic process affected by interaction of dissolved organic matter and calcium carbonate surfaces. Dry state inversion of aragonite to calcite or dry exsolution of Mg-calcite to calcite and dolomite will not be considered here.

Organic content and rock textures

Recent reef limestone from Bermuda--. A polished section of a Recent reef structure stained with Methylene Blue shows parallel lines of organic matter which seem to constitute the primary organic portion of encrusting algae. Another concentration of organic matter is in the pore space filled with silt- and clay-size carbonate mud. This pore filling is cemented by Mg-calcite(0.18). No visible uptake of stain was observed after H_2O_2 treatment, indicating that only organic matter was present and no clays.

Pleistocene conglomeratic limestone--. The sample was collected from Devonshire Formation, Devonshire Bay, Bermuda (Figure 23). This is believed to be an intertidal transgressive deposit (Land, 1967). It consists of primary minerals, aragonite and Mg-calcite, and is cemented by calcite at grain contacts through fresh water diagenesis. Methylene Blue uptake shows three characteristics: In some skeletal fragments, internal organic matter is stained blue, indicating proteinaceous material. In other fragments, pink stain shows SO_4^{2-} reactive sites of mucopolysaccharides or similar compounds. A blue coating surrounds the entire primary pore space and is only absent at cemented grain contacts. H_2O_2 treatment removed this coating and approximately 90% of the internal organic matter.

Pleistocene uncemented carbonate sediment--. The sample was collected from the Harrington Formation at Whalebone Bay, Bermuda. It consists of friable or completely uncemented carbonate sand, which was colored reddish brown by clay minerals and organic matter.

All fresh sediment particles were intensely stained by Methylene Blue; however, staining was markedly reduced after H_2O_2 treatment.

Upper Jurasic limestone from Comblanchien, Dijon, France--. Skeletal fragments and oolites are enclosed in micrite envelopes and are partly replaced by sparry calcite; lutitic ground mass is still present. Large sparry calcite crystals fill solution cavities and other pore spaces. Throughout the sample the micrite envolopes were uniformly stained by Methylene Blue (Figure 24). After H_2O_2 treatment, they were re-stainable, but at greatly reduced intensity. Perhaps the micrite envelope consists of organic coatings in the form of organo-clay complexes.

Figure 23. Conglomeratic limestone, Devonshire Formation, Devonshire Bay, Bermuda.

The location of Methylene Blue stainable layers are indicated by the arrows. These layers contain organic matter as well as clay minerals.

Figure 24

(a) The dark area shows the coarse recrystallization mosaic of a coral. Note that the individual polyps are filled with sediment and that only septae are recrystallized. Skeletal fragments and oolites(?) are not recrystallized. These are enclosed in a micrite envelope, which is visible as a white line. The micrite envelope as well as most of the unrecrystallized portion of the rock was stainable with Methylene Blue, thus indicating the presence of organic matter and clay minerals. The long dimension of the photograph represents 3.0 cm.

(b) Detail from Figure 24 (a) under polarized light and with gypsum plate shows the relationship between micrite envelope and recrystallization mosaic.

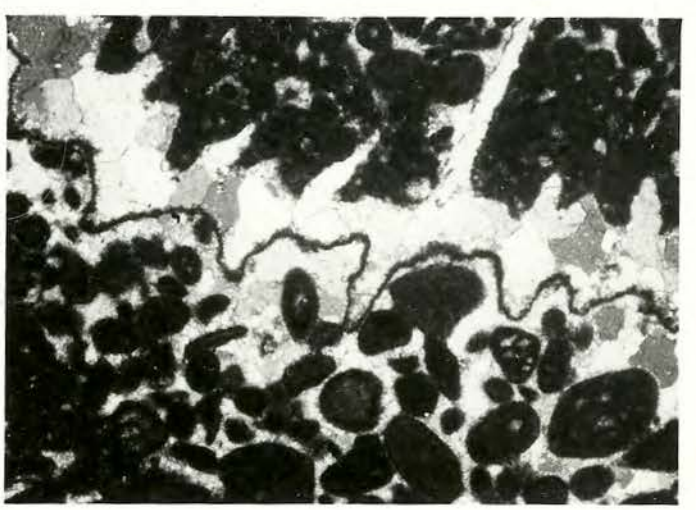


Figure 24 (b)

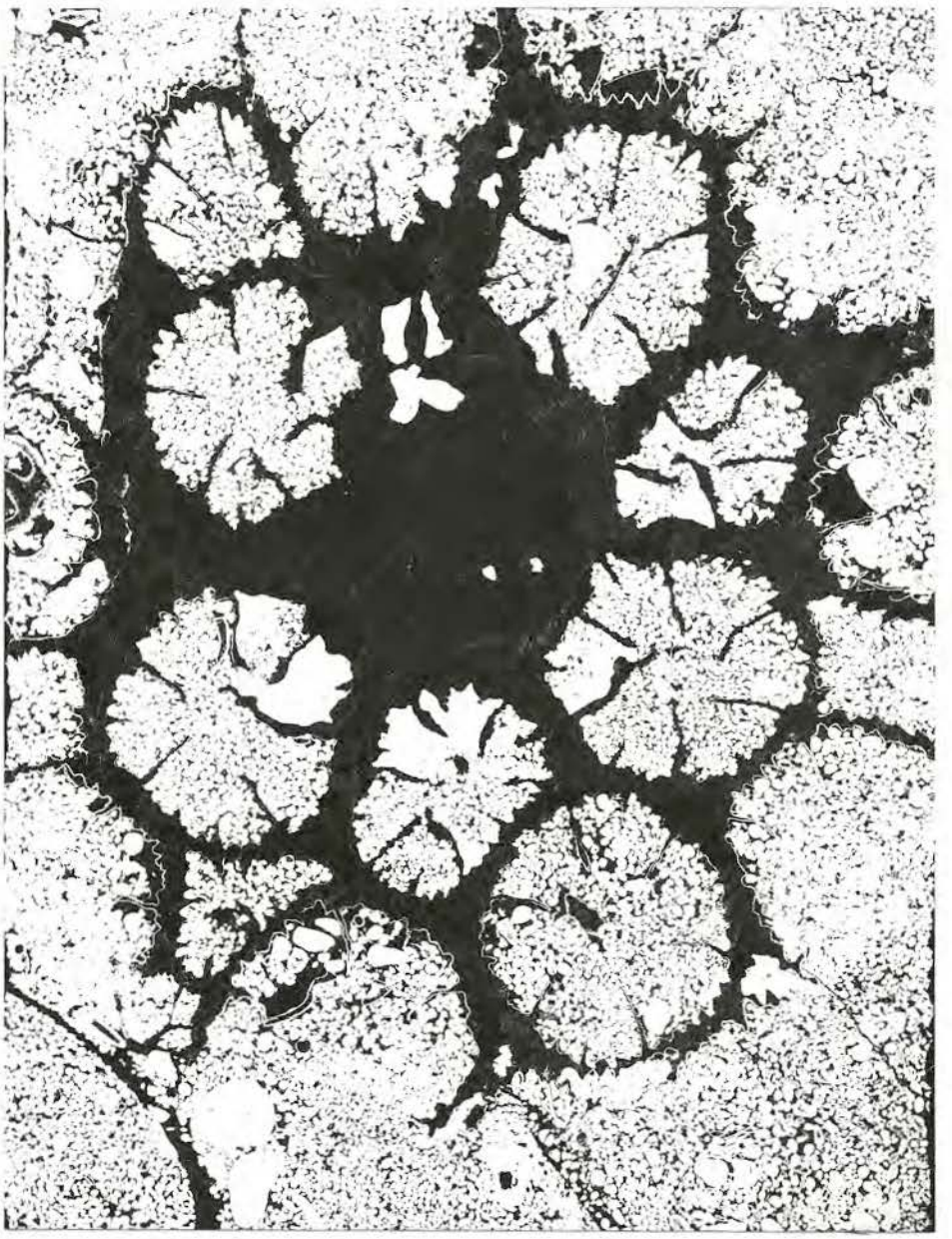


Figure 24 (a). Upper Jurassic limestone from Comblanchien, near Dijon, France.

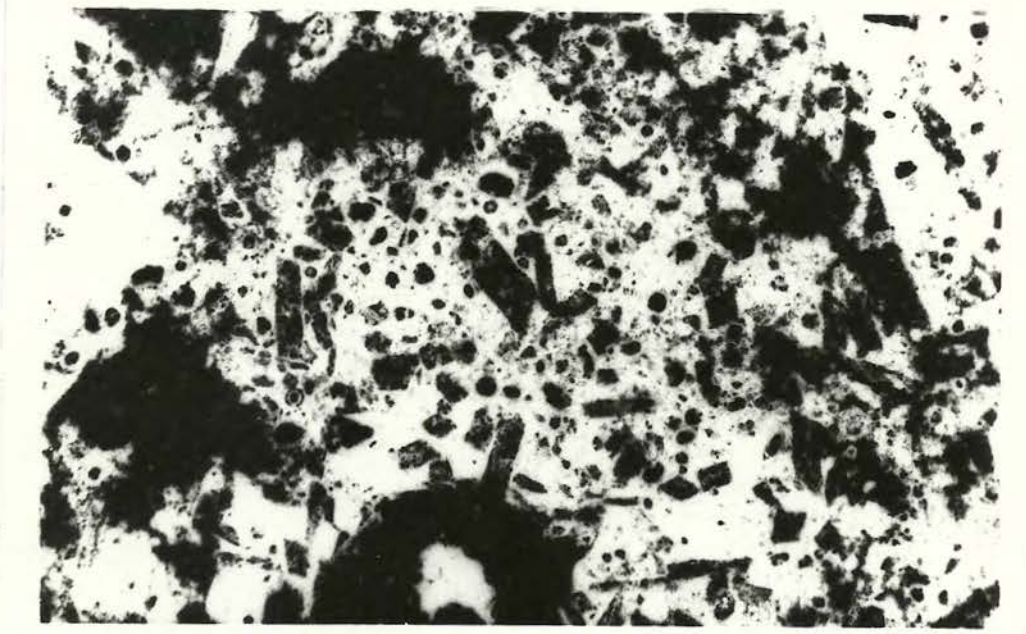


Figure 25. Mississippian dolomite from Indiana.

A large single crystal of dolomite fills the interlocking pore space. The entire black area of the photograph is a single crystal. The fine grained matrix was stainable with Methylene Blue, indicating the presence of organic matter and clay minerals.

Mississippian dolomite from Indiana--. A large single crystal of protodolomite fills the interlocking pore space of a lutitic groundmass; discrete areas of the matrix are stained by Methylene Blue. Some stained portions entirely surround pieces of matrix or line pore spaces which later were filled by the single crystal. H_2O_2 treatment reduced the intensity of staining. The insoluble residue fraction of this rock consists of quartz, illite, chlorite, kaolinite, feldspar(?), and organic matter. The uptake of Methylene Blue by the organic-free fraction was between 37% and 42% less than that of the total insoluble residue.

Interpretation

As noted in the introduction to this section, the uptake of Methylene Blue by clay minerals strongly interferes with direct determination of organic coatings. Not until a histochemical determination of organic matter can be found which is not affected by the presence of clay minerals can the results of this brief survey of organic content and rock textures show any significant petrological implications.

Primary and adsorbed organic matter of skeletal carbonate particles in Recent sediments and Pleistocene rocks can be determined by applying Methylene Blue staining techniques. The organic matter contains carboxyl-, phosphate-, and sulfate groups. It also shows the presence and exact location of clay minerals in carbonate rock constituents. Whether or not the stained organic portion and the clay mineral fraction can be distinguished, it is helpful to localize organo-clay associations on carbonate grains.

For example, the stained micrite envelopes of the Upper Jurassic limestone indicate that organo-clay associations on the surface of

skeletal and other carbonate particles inhibit grain enlargement. Recrystallization of other parts of the same rock is completed to a coarse calcite mosaic. (Note the large coral shown in Figure 24.) The micrite envelope is still visible at these parts of the rock, but in some places it is ruptured and missing, allowing diagenetic processes to take place.

There is no example which demonstrates the effect of organic coatings on the transformation of aragonite to calcite. Instead, the sample of cemented conglomeratic limestone from the Devonshire Formation, in which the original mineralogy is preserved, indicates that the absence of organic coatings induced precipitation of calcite cement. The outer surface of the calcite cement shows the presence of organo-clay associations, and these associations will probably affect the future processes of diagenesis.

Organo-clay associations prevent cementation of the carbonate particles in the sample from the Harrington Formation. Organo-clay coatings on the matrix and in the form of pore-space lining are perhaps responsible for the blocking of nucleation sites and causing the interstitial fluid to precipitate a single crystal of macroscopic dimensions, as shown in the sample of Mississippian dolomite.

The associations of organic matter and clay minerals with the surface of particles in carbonate rocks suggest a new aspect of organo-carbonate associations. The mechanism of association between clay-organo complexes and carbonate minerals is very likely of the same kind as described in this study. The effects on recrystallization and replacement processes are perhaps also similar to those postulated here.

V. CONCLUSION

Organo-carbonate associations in hexane and in distilled water systems can be described and quantitatively treated in detail. However, only incomplete conclusions can be made concerning their presence and effects in the natural environment of carbonate deposition. Inferences about past environments are, at best, guesses.

Stearic acid and albumin in simple, controlled experiments are physically and chemically adsorbed by carbonate minerals. However, the actual mechanisms in seawater for the association of calcite and "surface-active" dissolved compounds cannot be directly determined. Experiments at the air-seawater interface by other workers have shown that physical adsorption is a common process. Chemical adsorption is also indicated since preference is shown in experiments for calcium-stearic acid association rather than for magnesium and stearic acid. Members of the homologous series of fatty acids, fatty esters, and fatty alcohols behave similarly in defined adsorption systems (Traube's Rule; Traube, 1891). Therefore, preferential association of calcium and surface-active compounds is perhaps a general characteristic of most natural organo-mineral associations. Before such characteristics can be said to be true of all these associations, it is of great importance to know in what state organic compounds exist in seawater.

Fatty acids, fatty esters, and fatty alcohols are more concentrated than proteins in seawater and are therefore more important as interacting compounds than the protein fraction. It is almost certain that new interacting compounds will be found when more work is done on seawater composition.

The organic layers which are associated with calcite and dolomite surfaces in a hexane solvent system are probably arranged in a chain-like structure of stearic acid molecules on calcium sites. With water as solvent, the structure of a surface layer is more complicated and more ambiguous. Any particular structure proposed for organo-carbonate associations formed in seawater would be highly speculative.

Morphological comparison between natural organic aggregates enclosing carbonate grains and aggregates of albumin formed on calcite particles indicates that the organic matter in both examples is arranged in the form of a non-oriented thick coating on the solid surface. Organic matter in the form of organo-clay complexes in carbonate rocks forms protective coatings of unknown structure.

Calcium carbonate equilibration is influenced by at least three major phenomena -- physical isolation, solubility of surface complexes, and selective association of calcium and stearic acid.

Physical isolation of the mineral surface appears to prevent solution-solid equilibration. Most suspended carbonate minerals are enclosed by visible organic matter (Chave, 1965a, 1965b). Therefore, this "plastic bag" phenomenon is quite important in today's oceanic environment. The solubility of surface complexes may account for high calcium and carbonate activity products in seawater. It should be extremely interesting to synthesize and to isolate such organo-carbonate complexes. Enhanced magnesium dissolution from the calcite lattice is caused by selective association of organic matter with calcium sites.

No single phenomenon affecting the calcium carbonate equilibrium can be assigned to a single environment of deposition, nor is it expected that

a single process operates exclusively in a particular environment. More likely, any combination of effects caused by physical isolation, solubility of surface complexes, and selective organo-carbonate association inhibits simple calcium carbonate equilibration in nature. Such inhibition explains the apparent supersaturation of seawater with respect to calcite, the disequilibrium conditions between suspended carbonate minerals and seawater, and the lack of equilibration of most of the Recent carbonate mineral assemblages with interstitial waters.

Evidence is scarce for persistent effects of organo-carbonate associations on inorganic equilibration of ancient carbonate deposits. The presence of organo-carbonate association can be inferred from rock textures, but direct demonstration is hampered by interference from clay minerals, at least in the method used in this study.

Knowledge about stability conditions of organo-carbonate associations is clearly needed in order to unravel the diagenetic history of carbonate deposits and to deal with questions such as these:

What was the saturation state of ocean water with respect to calcite throughout the earth's history?

Was the saturation state related to organo-carbonate associations?

When did these associations first form?

How long have organo-carbonate associations affected the saturation state, carbonate deposition, and limestone textures?

What is the source of the organic matter?

Could evolution and abundance of marine life be correlated to the effects of organo-carbonate associations?

These questions are, of course, not within reach at the present time and with the present knowledge, but they may indicate a new direction of possible development in the study of carbonate deposition.

On the other hand, concrete information can be drawn from the analytical techniques developed during this study. The "critical calcite surface area" enables future workers to characterize the organo-chemical composition of seawater. If calcite proves to be a selective adsorbent, fatty acids and other compounds can be isolated from seawater for analytical investigation. These techniques may be supplemented by use of histological staining.

Organo-carbonate complexes containing phosphorus, halogens, and other elements provide a means for concentrating trace elements in sediments. Correns (1956) suggests that iodine and bromine accumulate as organically bound halogens. Iodine and bromine concentrations in limestones and silicious rocks (Graf, 1960; Walters, 1967) show that limestones are the more efficient in concentrating these elements, even though the total organic matter of silicious rocks is often higher than that of carbonate rocks. Perhaps sorption by carbonate particles is responsible for the greater concentrations of halogens in limestones, as compared to non-carbonate sedimentary rocks.

Obviously the geochemical behavior of calcium carbonate in Recent and ancient sedimentary environments cannot be explained by applying only simplified chemical models. In order to understand calcium carbonate geochemistry, one must recognize the deviations of natural behavior from idealized behavior. These deviations, in turn, may be explained by more complicated chemical models, as in this example of sorption processes.

APPENDIX

Appendix I

Surface area determination of carbonate minerals

The specific surface area of calcite, dolomite, and Mg-calcite was determined by argon adsorption after the method of Brunauer, Emmett, and Teller. The measurements for this study were made by Mr. Estaban Chornet using the facilities of the National Printing Ink Research Institute at Lehigh University, Bethlehem, Pennsylvania.

Outline of method --. Argon was contained in a calibrated system under known pressure. Preweighed amounts of powdered carbonate minerals were kept in a constant-temperature sample tube which was separated from the argon system by a stop-cock. The volume of the sample tube was calibrated and evacuated. The argon was admitted to the sample, and the volume of gas adsorbed was calculated from the pressure reading after equilibrium was attained. A series of different measurements at different pressures determined the adsorption isotherm. The isotherm is described by the BET equation:

(A1)
$$\frac{P_E}{V_A(P_o - P_E)} = \frac{1}{V_m \cdot C} + \frac{C - 1}{V_m \cdot C} \cdot \frac{P_E}{P_o}$$

P_E = Pressure at equilibrium
P_o^E = Pressure before equilibrium
V_A = Volume of gas adsorbed at STP per gram of solid
V_m = Volume of gas adsorbed at monolayer formation per gram solid
C = Constant
A = Avogadro's number = 6.023×10^{23}
V = Molar volume of an ideal gas = 22.414 cm^3 at STP
M = Molecular area of argon = 14.4 $Å^2$

A plot of $P_E/V_A(P_o-P_E)$ versus P_E/P_o gives a straight line relationship, where the intercept I is:

(A2) $$I = \frac{1}{V_m \cdot C}$$

and the slope S is:

(A3) $$S = \frac{C - 1}{V_m \cdot C}$$

Slope and intercept are graphically obtained from the plot. This yields two equations from which C and V_m can be evaluated:

(A4) $$V_m = \frac{1}{S + I}$$

The specific surface area is therefore:

(A5) $$\text{Area} = \frac{V_m \cdot M \cdot A}{V \cdot 10^{20}}$$

The results are in Table AI and the plots in Figures AI - AIII.

Table AI. Specific surface area determination of calcite, dolomite, and Mg-calcite.

CALCITE		DOLOMITE		MG-CALCITE	
P_E/P_o	$P_E/V_A(P_o-P_E)$	P_E/P_o	$P_E/V_A(P_o-P_E)$	P_E/P_o	$P_E/V_A(P_E-P_o)$
0.0429	1.1080	0.0279	0.2913	0.0139	0.1463
0.0697	0.6234	0.0616	0.4191	0.0461	0.2115
0.1043	0.6834	0.1043	0.6011	0.1123	0.4207
0.1486	0.9119	0.1515	0.8358	0.1758	0.6130
0.1963	1.1501	0.1991	1.0724	0.2370	0.8085
0.2375	1.3616	0.2535	1.3603	0.2947	0.9967
0.2752	1.5572	0.3020	1.5946	-	-
0.3203	1.7655	0.3456	1.8222	-	-

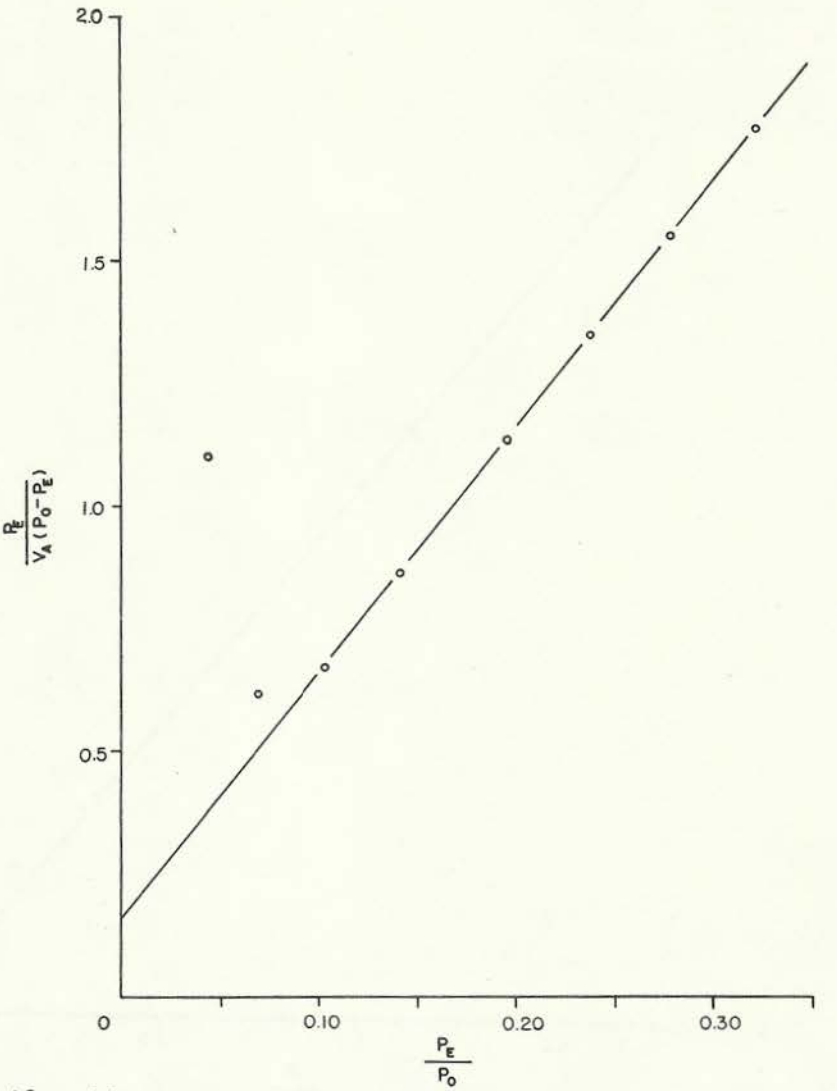


Figure A1. Adsorption of argon by calcite.

Slope	= 5.033
Intercept	= 0.16
V_m	= 0.193

Specific surface area = 0.714 m^2 per gram of calcite

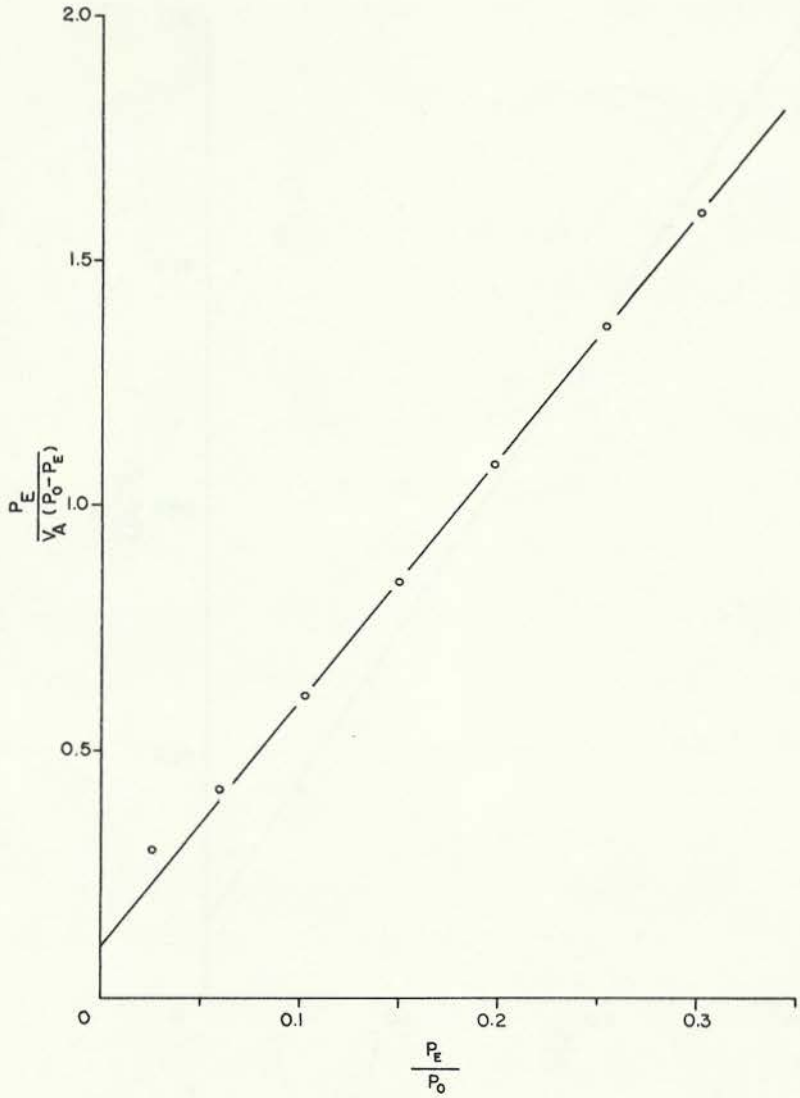


Figure A2. Adsorption of argon by dolomite.

Slope	= 4.884
Intercept	= 0.11
V_m	= 0.2004

Specific surface area = 0.743 m^2 per gram of dolomite

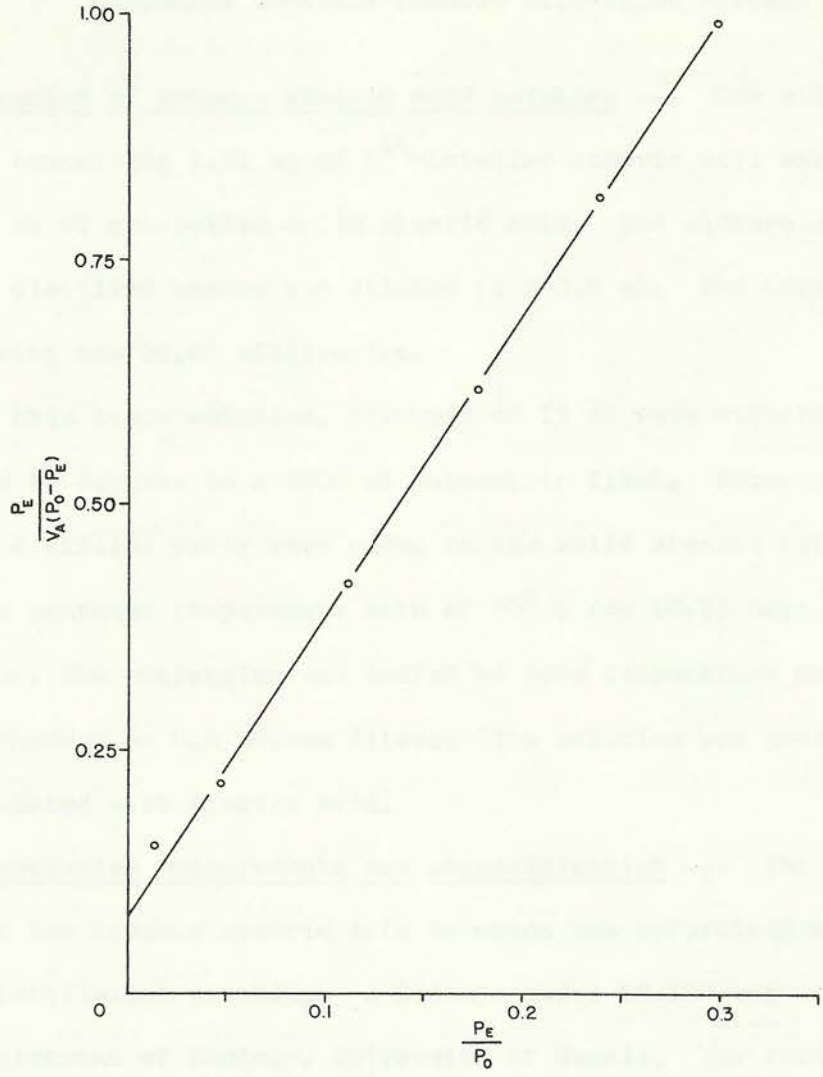


Figure A3. Adsorption of argon by Mg-calcite.

Slope	= 3.0775
Intercept	= 0.077
V_m	= 0.3175
Specific surface area	= 1.176 m^2 per gram of Mg-calcite

Appendix II.

Carbonate minerals-stearic acid-water systems

Preparation of aqueous stearic acid solution --. One millliliter of hexane containing 1.51 mg of C^{14}-labelled stearic acid was mixed with 21.5 mg of unlabelled solid stearic acid. The mixture was dissolved in distilled hexane and diluted to 100.0 ml. The total radioactivity was 20.67 millicuries.

From this stock solution, aliquots of 15 ml were withdrawn and evaporated to dryness in a 1000 ml volumetric flask. Subsequently, 800 ml of distilled water were added to the solid stearic acid and put into a constant temperature bath of 60° C for 10-15 days. After this period, the suspension was cooled to room temperature and filtered through an 0.8 micron filter. The solution was presumed to be saturated with stearic acid.

Concentration measurements and standardization --. The concentration of the aqueous stearic acid solution was determined by liquid scintillation counting. A Beckman model LS-100 was used at the Department of Zoology, University of Hawaii. The scintillation fluid consisted of dioxane containing 6 grams per liter PPO (= 2,5,-Diphenyloxazole), 0.2 gram per liter of POPOP (= 1,4,-Bis (2-(5-Phenyloxazolyl))-benzene), and 100 grams per liter of naphthalene. Figure A4 shows the calibration curves marked "C^{14} in water" which were established through counting a series of small volumes of initial stock solution, and Table AII shows the experimental data.

Table AII. Standardization of dissolved stearic acid in water and in hexane solution.

Volume of Solution Microliter	Stearic acid per milliliter of sample Milligram	Moles	Activity of stearic acid per milliliter of sample d/Minute	c/Minute	Error
150.0	$3.45 \cdot 10^{-3}$	$1.21 \cdot 10^{-8}$	$6.87 \cdot 10^{7}$	$3.813 \cdot 10^{5}$	0.2%
100.0	$2.30 \cdot 10^{-3}$	$8.09 \cdot 10^{-9}$	$4.58 \cdot 10^{7}$	$2.498 \cdot 10^{5}$	0.2%
50.0	$1.15 \cdot 10^{-3}$	$4.05 \cdot 10^{-9}$	$2.29 \cdot 10^{7}$	$1.176 \cdot 10^{5}$	0.3%
30.0	$6.90 \cdot 10^{-4}$	$2.42 \cdot 10^{-9}$	$1.37 \cdot 10^{7}$	$7.108 \cdot 10^{4}$	0.3%
10.0	$2.30 \cdot 10^{-4}$	$8.09 \cdot 10^{-10}$	$4.58 \cdot 10^{6}$	$2.465 \cdot 10^{4}$	0.7%
1.0	$2.30 \cdot 10^{-5}$	$8.09 \cdot 10^{-11}$	$4.58 \cdot 10^{5}$	$2.277 \cdot 10^{3}$	2.0%
0.5	$1.15 \cdot 10^{-5}$	$4.05 \cdot 10^{-11}$	$2.29 \cdot 10^{5}$	$1.174 \cdot 10^{3}$	3.0%
-	$3.3 \cdot 10^{-2}$	$1.16 \cdot 10^{-7}$	$2.8 \cdot 10^{7}$	$2.6 \cdot 10^{5}$	-
-	$6.0 \cdot 10^{-3}$	$2.11 \cdot 10^{-8}$	$5.2 \cdot 10^{6}$	$1.0 \cdot 10^{5}$	-

Adsorption experiments --. The aqueous stearic acid solution, which was presumably saturated, was diluted with increments of distilled water to lower concentrations. Duplicates of ten 25-ml samples were prepared. Preweighed amounts of powdered calcite and dolomite were added to each of the two series of samples. They were shaken intermittently and allowed to equilibrate with the atmosphere. After 20-30 hours, when the mineral particles had settled, one-milliliter aliqouts of supernatant solution were withdrawn for final concentration measurements of stearic acid. In the remaining suspension, pH and dissolved cations were measured. The data are in Table AIII.

Carbonate minerals-stearic acid-hexane system

Concentration measurements and standardization --. Two milliliters of hexane solution containing 3.02 mg of C^{14}-labelled stearic acid (= 41.32 millicuries) were mixed with 100.0 mg of unlabelled solid stearic acid, dissolved, and diluted with distilled hexane to

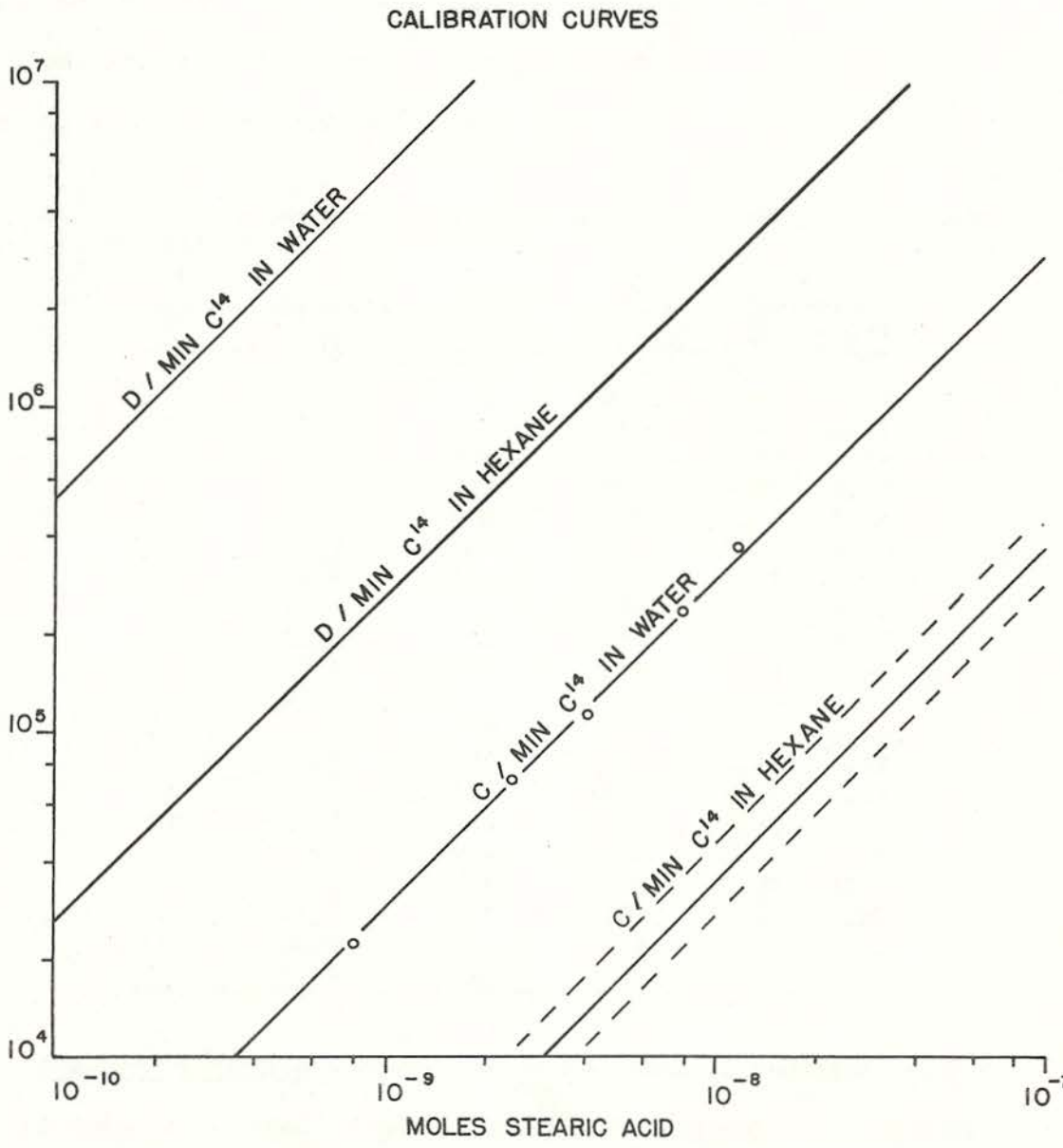


Figure A4. Calibration curves of stearic acid dissolved in water and in hexane.

100.0 ml. From this stock solution aliquots were withdrawn and evaporated. The solid stearic acid was weighed and redissolved in toluene solution containing PPO and POPOP as primary and secondary fluors for liquid scintillation counting. A Packard Tri-Carb counter with refrigerated sample system was used at the Bermuda Biological Station, St. George's, Bermuda. Figure A4 shows the calibration curves, which are marked "C^{14} in hexane".

Table AIII. Adsorption of stearic acid by calcite and dolomite from aqueous solution.

Sample #	Minerals mg	Initial c/min/ml	Final c/min/ml	Solution pH	Solution pCa^{++}
1	0.4	830	790	8.30	3.80
2	0.7	830	800	8.47	3.77
3	1.0	830	784	8.51	3.71
4	2.8	830	765	8.60	3.69
5	5.4	892	768	8.98	3.49
6	11.7	850	551	9.03	3.48
7	11.7	685	430	9.05	3.52
8	11.8	694	423	8.75	3.59
9	11.0	473	257	9.01	3.50
10	10.8	342	164	9.12	3.52
11	9.6	155	79	8.83	3.58
12	5.9	892	732	8.47	3.84
13	9.6	892	686	9.17	3.82
14	9.4	850	625	9.18	3.84
15	12.0	685	507	9.20	3.73
16	12.4	694	523	8.60	3.82
17	10.3	473	346	9.03	3.79
18	11.9	342	227	8.63	3.80
19	10.8	273	223	9.12	3.82
20	11.3	155	93	9.08	3.84

Adsorption experiments --. Various amounts of powdered calcite and dolomite were added to 5-ml samples of hexane solution containing stearic acid. The suspensions were centrifuged for 3-5 minutes in a clinical centrifuge, and one-milliliter aliquots were counted for the final stearic acid concentration. Experimental data are in Table AIV.

Table IV. Adsorption of stearic acid by calcite and dolomite from hexane solution.

Sample #	Minerals mg	Initial concentr. c/min/ml	Final concentr. c/min/ml
1	1.7	$2.316 \cdot 10^5$	$2.23 \cdot 10^5$
2	5.0	$2.316 \cdot 10^5$	$2.13 \cdot 10^5$
3	15.3	$2.316 \cdot 10^5$	$1.68 \cdot 10^5$
4	32.5	$2.316 \cdot 10^5$	$1.11 \cdot 10^5$
5	45.0	$2.316 \cdot 10^5$	$7.20 \cdot 10^4$
6	71.0	$2.316 \cdot 10^5$	$3.94 \cdot 10^4$
7	101.0	$2.316 \cdot 10^5$	$2.08 \cdot 10^4$
8	138.0	$2.316 \cdot 10^5$	$7.10 \cdot 10^3$
9	5.0	$2.316 \cdot 10^5$	$2.18 \cdot 10^5$
10	20.0	$2.316 \cdot 10^5$	$2.03 \cdot 10^5$
11	32.1	$2.316 \cdot 10^5$	$1.74 \cdot 10^5$
12	60.2	$2.316 \cdot 10^5$	$1.34 \cdot 10^5$
13	101.0	$2.316 \cdot 10^5$	$1.06 \cdot 10^5$
14	23.5	$8.30 \cdot 10^4$	$2.37 \cdot 10^4$
15	52.5	$8.30 \cdot 10^4$	$5.95 \cdot 10^3$
16	87.9	$8.30 \cdot 10^4$	$4.15 \cdot 10^3$
17	104.4	$8.30 \cdot 10^4$	$3.92 \cdot 10^3$
18	142.4	$8.30 \cdot 10^4$	$2.90 \cdot 10^3$
19	175.1	$8.30 \cdot 10^4$	$3.67 \cdot 10^3$

Carbonate Minerals-Albumin-Water System

Preparation and standardization of adsorbate solution--. Purified egg albumin was dissolved in distilled water. The solution was filtered and the concentration determined by evaporating 150 ml to dryness. It contained 22.3 mg albumin; therefore, the concentration of the albumin stock solution was 0.53 milligrams per liter.

Ten samples of 25 ml each were prepared in triplicate, containing 0,2,4,6,8,10,12,14,16,18 ml albumin stock solution. The concentration was measured spectrophotometrically on ninhydrin assays of 1 milliliter samples with Bausch and Lomb Spectronic 20.

Ninhydrin assay of albumin solution--. (After Clark, 1964.)

a. Ninhydrin solution: Four hundred mg of reagent-grade $SnCl_2 \cdot 2H_2O$ were dissolved in 250 ml H_2O (adjusted to pH 5 with NaOH or HCl, not NH_4OH). This solution was added to 250 ml methyl cellosolve containing 10 grams of dissolved ninhydrin.

b. Procedure: Three ml of ninhydrin solution were added to one ml of the unknown albumin solution and also to a distilled water blank. The contents of each tube were mixed and placed in a boiling water bath for twenty minutes. After heating, the test tubes were cooled and 10 ml of 50% aqueous n-proponal added to each sample with extreme care in mixing. After ten minutes, the optical densities at 570 milli-microns were measured against the blank (Figure A5).

Adsorption experiments--. The powdered carbonate samples were weighed to the nearest milligram and added to the albumin solution. Table AV gives the mineralogies and weights of the carbonate adsorbents, as well as the optical densities in per cent transmittance of the albumin solutions before and after adsorption. Figures A5 and A6 show the albumin concentration changes due to adsorption by carbonate minerals. The adsorption per gram of carbonate mineral was calculated from the concentration changes.

Table AV. Adsorption of albumin by various carbonate minerals from aqueous solution.

Sample #	Minerals mg	Initial concentration % Transmittance	mg	Final concentration % Transmittance
1	600 C	90.0	0.045	91.5
2	600 C	81.5	0.085	90.0
3	600 C	75.0	0.127	86.5
4	600 C	67.0	0.170	79.0
5	600 C	57.0	0.212	58.5
6	600 C	56.0	0.254	65.0
7	600 C	50.0	0.297	69.0
8	600 C	39.0	0.340	66.5
9	600 C	41.0	0.382	63.5
10	Blank	100.0	-	100.0
11	600 C	90.0	0.045	-
12	600 C	79.5	0.085	81.0
13	600 C	71.0	0.127	81.0
14	600 C	57.0	0.170	57.0
15	600 C	50.5	0.212	53.0
16	600 C	41.5	0.254	50.0
17	600 C	37.0	0.297	42.0
18	600 C	33.5	0.340	36.0
19	600 C	32.0	0.382	32.0
20	Blank	100.0	-	100.0
21	600 M	83.0	0.045	88.0
22	600 A	69.0	0.085	80.0
23	600 A	60.0	0.127	78.0
24	600 M	-	0.170	79.0
25	600 A	42.0	0.212	57.5
26	600 A	-	0.254	63.0
27	400 D	31.0	0.297	31.0
28	400 A	-	0.340	59.5
29	400 C	20.0	0.382	73.0
30	Blank	100.0	-	100.0

C = Calcite
M = Mg-calcite
D = Dolomite
A = Aragonite

Samples # 1-10 = pH 10
Samples # 11-20 = pH 7
Samples # 21-30 = pH 8 long term

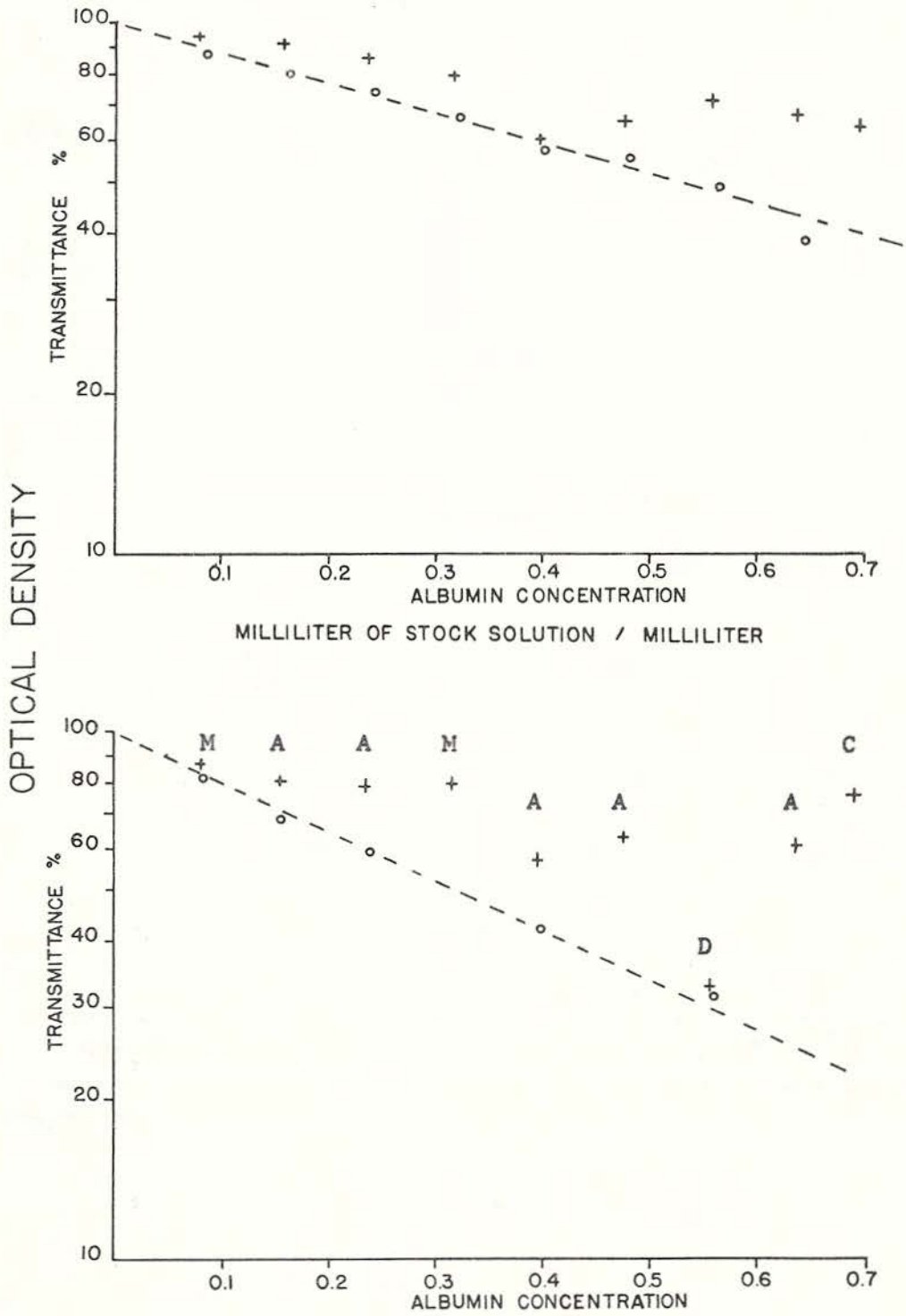


Figure A5. Adsorption of albumin by carbonate minerals from aqueous solution, initial versus final concentration measurements.

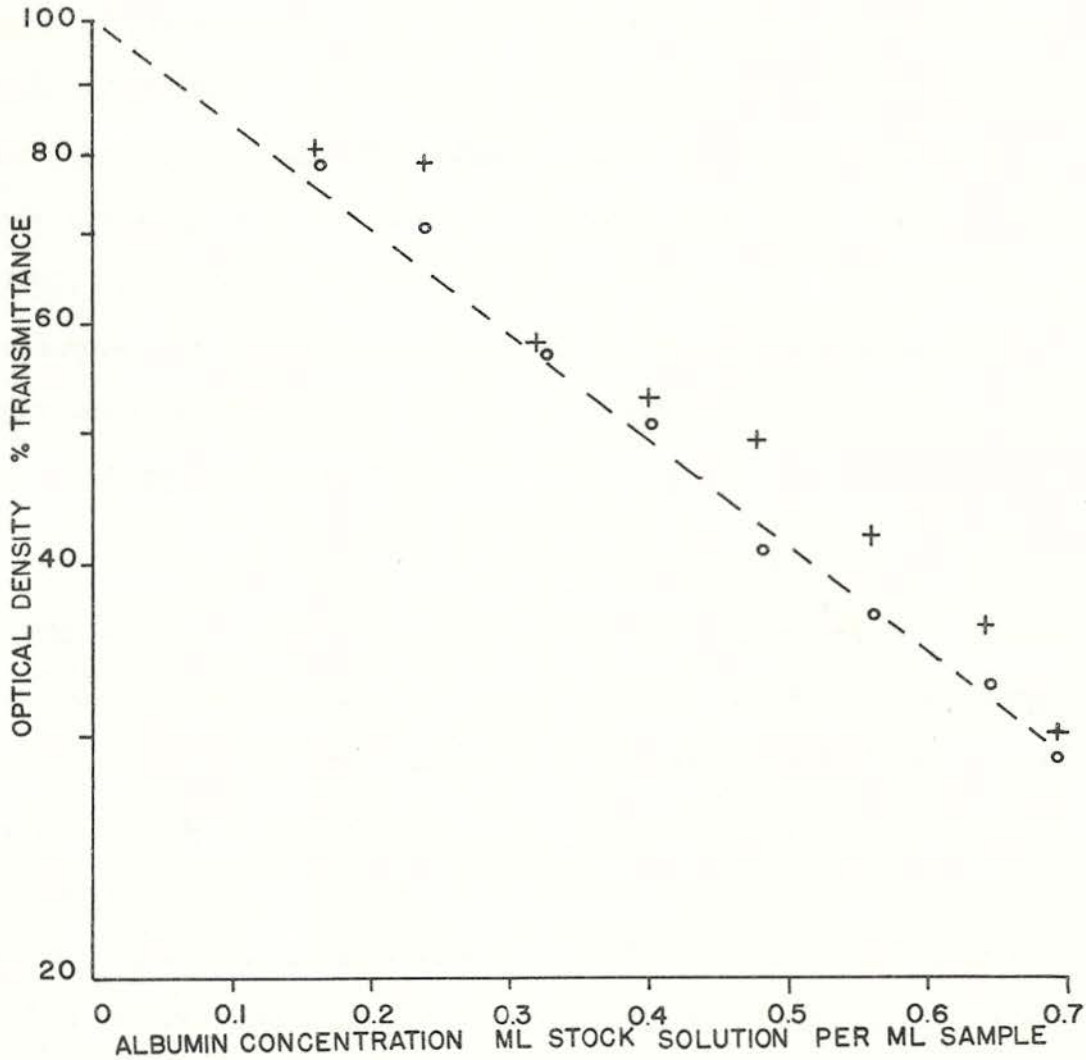


Figure A5. Adsorption of albumin by calcite from aqueous solution, initial versus final concentration measurements.

Appendix III

Seawater-calcite reactions

Calcite was reacted with seawater by placing six 200-ml samples of seawater on a multimagnetic stirrer and then adding preweighed amounts of ground calcite to five of the samples. The sixth sample served as a blank. PH measurements were taken at ten-minute intervals. A battery-operated Photovolt Model 180 pH-meter was used and standarized before and after each series of measurements with buffers of pH 4.01 and pH 7.00. The nominal precision of the instrument was 0.01 pH units. The experiments were terminated when the pH change of the samples was no longer any greater than that of the blank sample. The corrected readings are in Figures 11 and 12 of Chapter III.

Methylene Blue staining techniques

The samples to be stained were dried over silica gel in a dessicator. These included organic aggregates filtered from seawater, organically coated sediment particles, and polished limestone slabs. Porous rocks were impregnated with Epoxy before polishing. The staining solution contained 0.1% Methylene Blue and the pH was adjusted with NaOH to 9 $\pm$ 0.5. During the staining procedure, the samples were slightly agitated. The time required for staining was ten to twenty minutes. After staining, the samples were washed three times in an excess of distilled water of pH 9. When the wash water was completely clear, the samples were either air-dried or dehydrated in tertiary-butanol. It is advisable to permanently mount the specimens after staining.

Appendix IV

Carbonate sediments-seawater reactions

Preparation of undersaturated seawater--. CO_2 was bubbled through filtered seawater then mixed with supersaturated seawater until the desired pH was attained. These undersaturated solutions must always be prepared immediately before performing the sediment-seawater reactions since the pH changes due to loss of CO_2 after more than one hour.

Treatment of sediment--. As soon as possible after sampling, the insterstitial pH was measured by immersing the electrodes into the sediment. About 30 grams of sediment were then gently mixed with approximately 50 ml of undersaturated seawater (prepared as described above). This slurry was poured into a cone-shaped container which was resting in a larger vessel and which contained the pH-electrode. The sediment then settled around the tip of the pH-electrode. The calomel electrode extended into the space between the two reaction vessels which were electrolytically connected by seawater. The cone-shaped reaction vessel was entirely immersed as shown in Figure A6. The seawater-sediment interaction could be thus continuously monitored and recorded, if so desired. The pH of the undersaturated seawater should be as close to that of the interstitial water as possible to avoid pH changes due to mixing. Mixing effects were minimized by the preparation of a slurry and by pouring it slowly into the reaction vesse.

Peroxide treatment--. In order to remove organic matter, 50 grams of sediment were boiled in 30% H_2O_2 for 3-5 hours. The pH of hydrogen peroxide was adjusted to 8.5 $\pm$ .2 with NaOH. After treatment, the sediment was washed twice in 150 ml of distilled water (pH 8.5 $\pm$ .2)

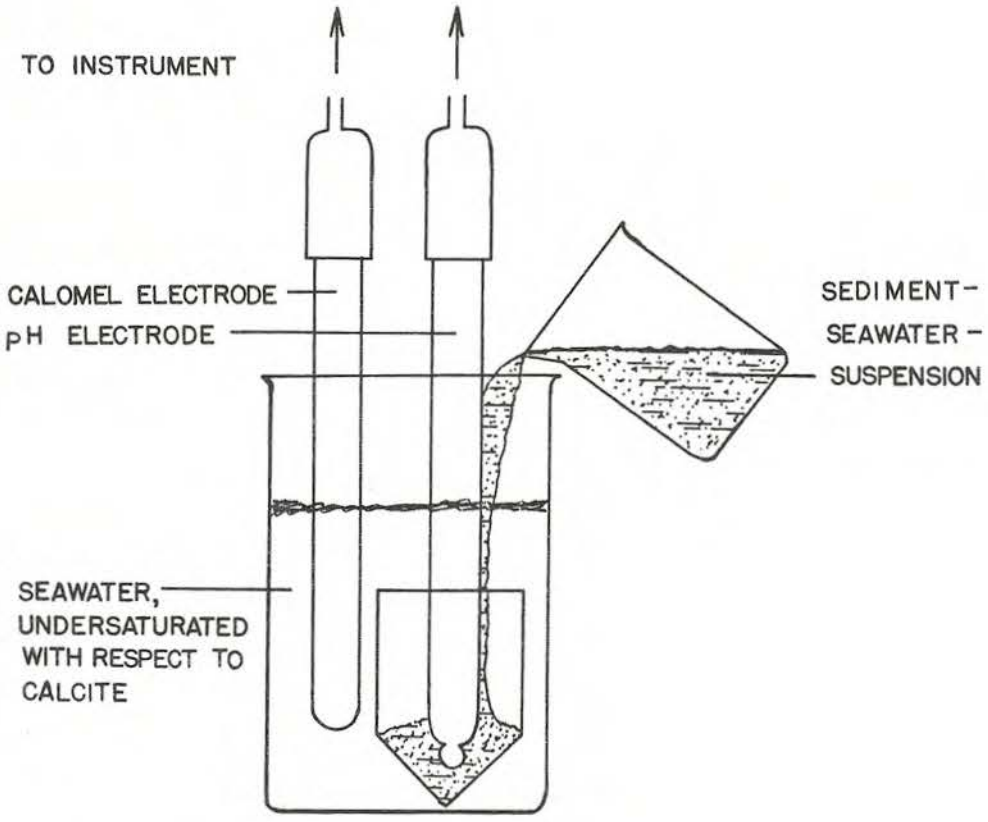


Figure A6. Instrumental arrangement for monitoring seawater-sediment reactions.

to remove H_2O_2 and three times with 50 ml of filtered seawater of pH 8.2. Then, the sediment was mixed with 50 ml of undersaturated seawater and the suspension poured into the reaction vessel. For fine-grained sediments, it is necessary to use a centrifuge during the washing procedures. A steady state pH was attained usually within twenty minutes. The experimental data of the seawater-sediment reactions are in Table XIV of Chapter IV.

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13. ABSTRACT

Dissolved organic compounds interact with the surface of calcium carbonate minerals and effect simple inorganic equilibration between solution and solid. Organo-carbonate associations form between stearic acid and calcite and dolomite, and between albumin and aragonite, calcite, and Mg-calcite.

When stearic acid interacts with these minerals in hexane solution, a complete monolayer forms on the calcite surface, and half of a layer forms on the dolomite surface. Interaction is restricted to the calcium sites of the solid and the carboxyl group of the stearic acid. When stearic acid and carbonate minerals interact in aqueous solution, the amount adsorbed is not sufficient to form a complete monolayer of pure stearic acid, although hydrated surface complexes appear to be large enough to completely cover the surface of the minerals.

At low concentrations in water, albumin forms a complete monolayer on carbonate minerals. At higher concentrations, multilayers or unoriented aggregates form.

Organo-carbonate associations affect the calcium carbonate equilibrium in solution by physically isolating the mineral surface and by reducing the surface free energy of the solid. At low calcite to seawater ratios, the adsorbed surface-active organic matter is visible on the surface of calcite and can be stained by Methylene Blue. The artificially produced organic coatings look the same as those observed on natural suspended carbonate minerals.

Surface seawater, deep water, and interstitial water show inorganic equilibration at different calcite to seawater ratios. These ratios are constant for one seawater sample whether equilibrium is approached from under- or oversaturation.

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